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Inorganic Chemistry

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A TEXT-BOOK

OF

INORGANIC CHEMISTRY

DESCRIPTIVE, THEORETICAL, AND PRACTICAL
A MANUAL FOR ADVANCED STUDENTS

PART II

METALLIC ELEMENTS AND QUALITATIVE ANALYSIS

BY

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PREFACE.

THE favorable reception that has been given to Part I. of this work has encouraged the author to publish Part II., which completes the volume. The same general method of presenting the subject that was adopted for Part I. has been followed in this part.

The treatment given the classification of the elements by the periodic law it is hoped will prove sufficiently extended to meet the needs of students using this work, although many points in reference to it have not been spoken of. Much work in collecting and bringing periodic facts together has been merely suggested, and then left for the student (and instructor) to do, in the hope that it will stimulate a study of these facts, and thus impress them on the mind of the learner.

The writer believes that quantitative study should begin early in a course in chemistry, and so much of this has been introduced as experience has shown beginners can profitably do.

Qualitative chemical analysis can be made a most valuable aid in education if it does not degenerate into a mere corroboration of directions. It is of doubtful utility if the student merely learns a system of analysis. The main facts to be used should be known to the learner so that they may become the instruments by which results are reasoned out, which may be afterwards combined by experience. The facts, therefore, come first, and the writer believes that the student should

have these facts at his command when he begins this study, in spite of the fact that it requires considerable effort to reach this result. It is not meant that the student should commit to memory schemes for analysis, but that he should have in mind the main facts upon which these schemes rest. This should be true without reference to the ultimate object of the student who is pursuing the study. If he is to use the methods as a practical chemist, this knowledge is certainly of the utmost importance. The work of a practical chemist is not a trade, but is the application of scientific knowledge to the problems of civilization, and hence the knowledge of the science must precede its application.

It is needless to say that the treatment of the subject here is intended to be of an elementary character. Rare elements are not included, since they are never studied by the beginner.

In the hope that both instructors and students of chemistry may find something helpful in this work, it is presented for their consideration.

ALFRED A. BENNETT.

AMES, Iowa, August, 1894.

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INORGANIC CHEMISTRY.

THE METALS.

INTRODUCTORY.

THE division of the elements into metals and non-metals has been a recognized classification from the early times. The elements included under the term *metal* are more numerous than are the non-metals or acid-forming elements, although many of them are only found in very small quantities.

The elements that have been studied in Part I. of this work all form compounds with hydrogen, with the exception of potassium and sodium. These elements number sixteen. Their compounds with hydrogen are not stable in all cases, and they are not all of them readily formed. The metals cannot, on the other hand, be said to form any stable compounds with hydrogen.

The division of the elements just made is not clearly marked, especially when a careful study of them is made. Such a study would show that some of the non-metals possess many of the properties of the metals. For example, arsenic and antimony have many physical and chemical properties in common with the metals, and will be studied from both standpoints. The distinction is not difficult to make between certain of the metals and non-metals, but a strict classification into these two series is not possible.

Perhaps the most characteristic property of the non-metals is

that of producing acid compounds with hydrogen and oxygen, and in a few cases with hydrogen alone; *i.e.* their hydroxyl compounds are acid in the more general sense of the term. The hydrogen of these compounds can be replaced by the metals, forming the class of compounds called salts.

The term *metal* was applied by the Greeks to six elements; namely, silver, iron, tin, lead, copper, and gold. The name *metal* was given to these substances since they were found in mines. The word is said to signify a mine.

Physical Properties (generally characteristic). — The early chemists considered such properties as hardness, lustre, and malleability characteristic of metals. Later such properties as conductibility of heat and electricity and the arrangement of these elements at the positive pole of a battery under the proper conditions were added to the list as characteristic properties.

It may be well to note here that when an electric current is passed through a body, whether simple or compound, two classes of effects are noticeable. (*a*) The body undergoes no chemical change; (*b*) the bodies undergo a chemical change which accompanies the passage of the current of electricity. The bodies will be more or less heated in (*a*), depending on the substance. The bodies (*b*) are compounds, while the first class consists of elements and alloys. In case of the compound bodies, they are separated into at least two parts, one of which is gathered at the positive pole of the current, and the other at the negative pole. The metals and metallic groups and hydrogen belong to the first class, and the non-metals and the acid groups belong to the other class.[1] Whether or not these parts are finally free depends on their chemical character and the condition under which the action took place. For example, if a potassium compound is subjected to electrolysis (if the salt

[1] See Otswald's *General Chemistry*, p. 270.

or compound is fused, and the compound surrounds the poles of the battery), potassium is set free, and also the element, or group of elements, combined with it. Potassium hydroxid becomes potassium, water, and oxygen. If the substance is sodium sulfate, and it is a water solution, the sodium is set free, and the acid group, SO_4, breaks up into SO_3 and O. But these substances do not exist free under these conditions. The sodium reacts with the water in the usual way, and free hydrogen and sodium hydroxid are found at the negative pole. The sulfur trioxid reacts with water, and hence sulfuric acid and oxygen are found at the positive pole. If the compound is binary, then the elements are found at the poles of the current; namely, the metals at the negative, and the non-metals at the positive pole, the secondary actions depending upon the conditions just named.

Another fact in reference to electrolysis is that in the simultaneous decomposition of compounds the amounts of the elements set free are in the same ratio as are the valences of the elements, taking hydrogen as unity. For example, if 1 g. of hydrogen is set free in a given time by a current of electricity, the same current will set free 23 g. of sodium, 107.7 g. of silver, and 31.6 g. of copper from cupric nitrate, and 63.3 g. from a cuprous salt. These facts are confirmatory of the valence of an element which may have been determined by other processes.

If certain of the non-metallic elements are compared with particular metallic elements, they are readily distinguished by their physical properties. For example, ordinary carbon can be readily distinguished from iron by the properties just mentioned, while other elements, like bismuth and antimony, are not so easily identified by these properties alone. The metals differ widely among themselves in reference to both their physical and chemical properties. These facts will be discovered as the study of the metals progresses. The classification of the ele-

ments into metals and non-metals is used only as a convenient division for study. The further scientific classification of elements is left until the study of the same is complete, since the most valuable classification can best be made after a general knowledge of all the elements has been gained. The classification to be used in the study that follows is the ordinary one employed in qualitative analysis, depending mainly on the solubility of certain salts of the metals.

Alloys and Amalgams. — Metals act chemically towards each other in a manner similar to the action of many of the non-metals on each other; *i.e.* they form weak combinations. In case of the non-metals, these combination products are called true chemical compounds, since, in general, the laws of constant and multiple proportion are followed. The metals are all solids (excepting mercury), and do not generally react with each other until they are heated, and usually require a state of fusion. Apparently the compounds formed do not obey the laws of Dalton, but mix or unite in all proportions. Such combinations are called alloys. Mercury unites with many of the metals without the application of heat, its liquid condition evidently serving to bring the substances into more intimate contact. These alloys are called amalgams. The alloys are all solid, if we except some of the amalgams in which there is an excess of mercury. Even in such cases, the excess of mercury can be separated out by forcing it through chamois skin. Recent examinations of alloys seem to show that they are, in many cases at least, definite compounds held in solution, as it were, in an excess of one of the metals. Definite crystalline compounds have been made between several of the elements. (See under SOLUTION, page 250.) In most cases, the alloys present many new properties, such as the lowering of the boiling and fusing points, color, hardness, etc. (See under alloys of the various metals.)

Methods and Order of Study of the Metals. — Each element

will be taken up under nearly the same heads as were the non-metals, namely: —

(*a*) Occurrence and distribution in nature.
(*b*) Sources and methods of preparation.
(*c*) Experimental study of the element.
(*d*) Physical and chemical properties.
(*e*) Name and history.
(*f*) Atomic mass and valence.
(*g*) Uses.
(*h*) Compounds of. — Sources of, general and particular.
  (1) With oxygen.
  (2) Hydroxyl.
  (3) Salts. — How produced. — Same topics as for an element.
(*i*) Actions of one salt upon another. — Solubility of salts.

SILVER.

Occurrence and Distribution. — Silver does not usually occur in nature in a free condition. It occurs principally combined with sulfur, chlorin, bromin, and iodin. It is usually found combined with sulfur and mixed with, or accompanied by other sulfids, such as lead and copper sulfids.

Native silver has been found in quite large masses, varying in quantity from about 375 kg. down to minute grains. However, most of the silver of the world is obtained from its native compound. The native silver nearly always contains small amounts of other metals such as gold, copper, antimony, and platinum.

The principal localities for silver ores are the Rocky Mountain regions in the United States, Mexico, South America, the Altai Mountains, Saxony, and Hungary.

Definition of the Terms Mineral and Ore. — Most of the

metallic elements occur in nature in combination, quite generally united with sulfur. These compounds or any simple inorganic substance found in nature are called minerals. Many substances that are of organic origin, yet have undergone such change as to lose their organic character, are included under this term. It is common to speak of mineral oil, waters, coal, etc.

A single mineral substance is quite rarely found pure in any large quantities, but it is often intimately mixed with many other minerals. These, more or less complex mixtures, if they serve as a source of some element or of some compound, are called ores. For example, silver ore may be silver sulfid so far as the source of the silver is concerned, but it contains, nearly always, other sulfids such as copper, lead, and arsenic sulfids. The composition of some of these ores is represented by such formulæ, as $(AgCu)_9(SbAs)S_6$, called polybasite; $(AgCu)_2S$, called silver-copper glance; Ag_5SbS_4, Stephanite. These ores are more or less mixed with the rock that forms the walls of the veins in which they are found.

Sources and Methods of Preparation. — Silver is principally obtained from its sulfid or chlorid ore. Large quantities of silver are obtained from galenite, an ore of lead consisting mainly of lead sulfid (which see).

The method of preparation of silver depends on the composition and character of the ore from which it is to be obtained. The particular description of apparatus and method of preparation belongs to metallurgy. In this work only the outlines of the methods will be given, and only those parts that are connected with the chemistry of the process. The ores that will be noticed are: —

(*a*) Those that contain native silver.

(*b*) Those that contain silver sulfid and no lead, or but little.

(*c*) Those that contain a little silver sulfid and much lead sulfid.

(*d*) Those that contain silver chlorid or a halogen salt of silver.

(*a*) Native silver is extracted by mixing the finely ground ore with mercury. This amalgamates with the silver, and with sufficient mercury forms a liquid amalgam which is readily separated from the foreign material of the ore. The mercury is driven off by heat and recondensed, the silver remains behind pure so far as the mercury is concerned.

(*b*) These ores are usually treated by one of two methods, depending on conditions in which the ore is found. Only the general facts can be given in either case.

(1) The amalgamation process.

By this method the ore is roasted after having been ground to a fine powder and thoroughly mixed with common salt. Suppose the ore to be Stephanite, Ag_5SbS_4, what changes are likely to occur as a result of this treatment? (See properties of silver and antimony.) The antimony and sulfur will be oxidized, a portion of the sulfur escaping as sulfur dioxid, and other portions uniting with the sodium of the common salt forming sodium sulfate. The chlorin of the salt unites with the silver, forming silver chlorid (which see). This mass of material containing the silver as silver chlorid, is next transferred to a rotating barrel, and mercury, pieces of iron, and water are added. This mixture is thoroughly stirred by the revolving of the barrel. The chief chemical action consists in setting the silver free and amalgamating it with the mercury, and the union of the iron with the chlorin of the chlorid, which is done by the combined action of the iron and mercury, the water serving to dissolve out the soluble compounds that are formed and thus bringing the chlorid in contact with the iron and mercury. The silver is obtained from the amalgam as described in (*a*). Sometimes the amalgamating is done along with the chlorination of the silver. The ore is ground to a very fine powder and mixed with salt and oxidized copper

pyrites, or native copper sulfid. Mercury is slowly added to this mixture, which results in the formation of an amalgam containing the silver. This process requires less expenditure of fuel, and is adapted to regions where fuel is not easily or cheaply procured.

(2) By the second process the silver is alloyed with lead, and this is freed from the lead by cupellation. (See under LEAD.)

(*c*) Ores included under this head include the argentiferous lead ores, and the treatment is the same as is given under lead ores up to the point of separation of the lead from the silver, when Pattison's or a modified Parkes' process is used, which are described under lead.

(*d*) The halogen ores are readily worked by the amalgamating process (*a*).

Experimental Study, No. 1. — (*a*) Examine a piece of pure silver and note such physical properties as color, odor, taste, and conductibility of heat. Heat one edge of a silver coin in the flame of the lamp, holding it in the fingers. If possible compare its conductibility with that of several other metals, using rods of the same size. Heat a bit of silver in the deflagrating-spoon as hot as the lamp will heat it. Does it fuse?

(*b*) Heat a piece of the silver in the air. This shows what as to its chemical relation to oxygen? Use ozone in place of air. Explain the difference in the results.

(*c*) Lay a piece of sulfur on a silver coin and leave it for a half-hour. Next heat the coin with the sulfur on it. Explain.

(*d*) Place a few crystals of iodin in a narrow hard glass tube and place on them a small piece of silver or, better, powdered silver. Heat the tube, converting the iodin into vapor. What is the effect on the silver? From this result what could you predict about the action of the other halogens on silver?

(*e*) Treat separately in the test-tube small pieces of silver with hydrochloric, sulfuric, and nitric acid. Use heat.[1] Note the effect of each acid. Use the sulfuric acid in its dilute solution (1 of acid to 1 of water) and in its concentrated form. In case of the nitric acid note particularly what gases escape. How does nitric acid act on matter generally? (See under study of nitric acid.) Evaporate this solution to dryness, being careful not to overheat the residue. (In evaporating solutions to dryness, overheating as the last portions of the liquid escape can be avoided by placing the evaporating-dish high above the flame, so that an upward current of hot gases will surround the dish.) Redissolve and allow the salt to crystallize. What is the name of the compound? Write the reaction for the action of nitric acid. Note the difference in the action of the dilute and concentrated sulfuric acid. What gas escapes when the concentrated acid is used? (Compare with the action of sulfuric acid on copper, Part I., page 225.) Write and explain the reaction.

(*f*) Heat a few pieces of the crystals of silver nitrate produced in (*e*) in a test-tube. What escapes? What is left in the tube?

(*g*) Place a piece of zinc in 5 cc. of a solution of silver nitrate and note the deposit after it has stood for an hour or more. Filter it out and fuse it on charcoal, covering it with sodium carbonate. Has the zinc changed? Where is it? After the action is complete, evaporate to dryness (a piece of zinc being always left in the solution). Examine the residue. Is it silver nitrate? Explain the change. Dissolve some of the residue and test for nitric acid (see page 255, Part I.). What do the facts here established show? Heat some of the residue on charcoal. Is silver set free?

[1] It is understood that the sulfuric acid usually supplied to students is the concentrated acid of commerce, and that the other two acids are about 20 per cent solutions.

(*h*) Place a weighed piece of zinc (say .5 g.) in 20 cc. of a solution of silver nitrate. Warm, and add more silver nitrate if necessary to react with all of the zinc. When the action is complete, filter out the deposit and wash it entirely free from silver nitrate. (Filtrate should give no precipitate with HCl.) Dry thoroughly, and weigh on the filter paper, using balanced papers. Compare the quantity of zinc used with the silver set free. Suppose the zinc is 65, what is the corresponding amount of silver?

(*i*) Carefully weigh about 1.5 g. pure, dry silver nitrate, and place it in a dry porcelain crucible, the mass of which is known. Heat the crucible until the nitrate is completely decomposed. (Be careful and not allow any of the nitrate to be thrown out by spurting.) Note what gases escape. Test them with a red-hot coal. What are the gases? What is the effect of heat on nitric acid and nitrates? Cool the crucible and weigh it, and thus determine the amount of metallic silver left, and the amount of gaseous matter that has escaped. Suppose the gaseous products to be 14 parts of nitrogen and 47.88 parts of oxygen, what amount does this give for the silver?

Physical Properties. — Silver when chemically pure is of a peculiar white color. This color is so characteristic that other substances resembling it in color are described as silvery white. When it is finely powdered or when it is deposited from its salts by means of zinc or other metals, it is black to gray in color. Although it is not very hard, it is sufficiently so to take a high polish. It has a specific gravity of 10.5. When heated to about 950° it fuses, and at very high temperatures (like those of the oxy-hydrogen flame, or of the electric arc) it is converted into a vapor, the density of which, however, has not been determined. Silver is a very ductile and malleable metal. It has been rolled into sheets .000254 mm. in thickness, and it is so ductile that 1 g. of the metal can be drawn into a wire over one mile in length (6173 ft.). Silver is a highly tenacious

metal; a wire 2 mm. in diameter requires a force of 85 kg. to break it. It takes the first place among metals as a conductor of heat and electricity.

Chemical Properties. — Silver is one of the few elements that have but little affinity for oxygen. It does not oxidize at all when heated in the atmosphere or even in pure oxygen. Ozone attacks it, however, at ordinary temperature, producing the peroxid (AgO). When silver is fused in the presence of oxygen, the latter is absorbed in the proportion of 22 volumes of oxygen to one volume of silver. The gas escapes when the metal solidifies. The peculiarity of this property is emphasized when the fact is considered, that in the presence of metallic impurities such as gold and lead this action is entirely destroyed. Silver has great affinity for sulfur either when free or when it is combined as hydrogen sulfid (H_2S), forming silver sulfid. Thus silver blackens when exposed to the air from the sulfur of the hydrogen sulfid commonly present. It is readily attacked by the halogens, forming the compound corresponding to the halogen used.

It is not attacked by the alkalis, and for this reason silver dishes are used to concentrate alkali solutions and to fuse the alkali substances that attack other vessels that are commonly used for similar purposes.

Silver is only slightly attacked by hydrochloric acid, owing to the fact that the compound formed, silver chlorid, is insoluble under the conditions and forms more or less of an adherent coating over the silver, preventing the acid from coming in contact with it. Hydrogen is set free. Sulfuric acid only slowly dissolves it in the cold, if at all, but when heated to a high temperature it is dissolved, forming silver sulfate. At this high temperature the hydrogen that is set free reduces the sulfuric acid to sulfur dioxid (SO_2) and water. The reaction is similar to that for copper given on page 255, Part I.

Nitric acid readily dissolves silver, forming silver nitrate,

($AgNo_3$). The action is, in general, the same as that of nitric acid on the other metals; *i.e.* the metal is first oxidized, and in this case the oxid is converted into the nitrate by the excess of the acid and dissolved in the water present. The acid used in the oxidation is converted into nitric oxid (NO), water, the excess of oxygen uniting with the silver. (See OXIDATION AND REDUCTION, page 272, Part I.)

Name and History. — From the facts that silver occurs native and that it can be readily separated from its ores, it has been known from the earliest times. The word *silver* signifies the shining one. It was also associated with the moon by the alchemist, and called luna. This fact is preserved in the name *lunar caustic* which silver nitrate still retains. The symbol, Ag, is derived from *argentum* the Latin word for silver, which also signifies white or shining.

Atomic Mass or Equivalent, and Valence. — From the examinations made under (*h*) it is shown that .9532+ g. of silver is always found in 1.5 g. of silver nitrate, or that there escapes .5467+ g. of nitrogen and oxygen. If these elements are represented by 14 and 47.88 respectively, the amount of these elements becomes 61.88, and the corresponding amount of silver is 107.89+. Now we know that this number of parts of nitrogen and oxygen in nitric acid corresponds to one part of hydrogen; and since silver has taken the place of this hydrogen, it is the amount of silver that corresponds to one atom of hydrogen. When other salts of silver are examined, it is found that this is the amount of silver that always corresponds to one part (atom) of hydrogen. Other metals, like zinc, take the place of silver in its salts, but it is always 107.9 parts of silver that is replaced for a corresponding amount of metal. For zinc, the number of parts necessary to set free 107.9 parts of silver is 32.7; for magnesium it is 12.2; etc. The number of parts of the metals just mentioned corresponds to one part (atom) of hydrogen.

When silver forms salts with acids containing two or three atoms of hydrogen, 107.9 parts of silver replace each atom. For example, in silver sulfate 2(107.9) parts of silver are united with 32 parts of sulfur and 64 parts of oxygen. Much study has been made of the compound of silver and chlorin, and all these results when brought together show that 107.9 parts of silver are combined with 35.37 parts of chlorin or one atom of chlorin. Other amounts of silver in compounds are always whole multiples of this number 107.9 when reduced to this basis of 35.37 parts of chlorin, or 31.96 parts of sulfur and 15.96 parts of oxygen.

This number, 107.9, is, therefore, the exchange equivalent of silver. The atomic mass of the element cannot be determined by the method employed for gaseous substances, since it forms no compounds whose vapor density has been determined. The atomic mass is, therefore, either 107.9 or some multiple of the same. The study just described points towards this number as the true one.

Law of Dulong and Petit. — About the year 1819, Dulong and Petit, two French physicists, as the result of their examination of the specific heat of many of the solid elements, found that there was a fairly constant relation between their specific heats and the accepted atomic mass of these elements. They found if the number expressing the specific heats of the elements examined be multiplied by the atomic masses of these elements that the product in each case was the same number or so nearly the same number that it was considered to be the same. The slight variability in this product for the various elements can be readily accounted for when the imperfections in methods for the determination of specific heat and atomic masses, that were in use at that time, are considered. This average number is 6.3. If it is granted that this relation between the specific heat and atomic mass exist, it becomes a simple problem to determine the atomic mass of the solid

elements. Knowing the specific heat of an element, it is only necessary to divide 6.3 by this number to determine the other term, the atomic mass. The determination of the specific heat of solid substances is easily within the range of experimental determination although the errors of such determinations are measurable. Applying this law to the metal silver, it gives an atomic mass agreeing very closely with the number 107.9. Other methods for the determination of the atomic mass of silver have been used, but they all lead to this one number, 107.9.

In the general application of the law of specific heat there are several apparent exceptions. These exceptions have been found, however, to be susceptible of explanation in the light of facts that have been discovered by a careful study of these elements.

It has been shown that the facts of temperature must be considered in connection with these determinations; that the specific heat varies, up to certain limits, with the temperature, but that there is a temperature for each element when each of them follows the law quite closely. This fact is illustrated by the element carbon, as graphite, which at ordinary temperatures has a specific heat of .174. If it is determined at a temperature of 600°, it becomes .460. When these numbers are multiplied by 12, the products are 2.048 and 5.52; the latter number approximating closely to the constant, 6.3.

A quantitative analysis of silver chlorid shows that for every 107.9 parts of silver present in the compound, there are 35.37 parts of chlorin, or one atom. The chlorid may be regarded, therefore, as formed from hydrogen chlorid by the replacement of its one atom of hydrogen by one atom of silver. The valence of silver is, therefore, unity, or it is univalent. This is also shown by its other salts; for example, silver sulfate. If silver is univalent, silver sulfate should contain 215.8 parts of silver to 96 parts of sulfur and oxygen. Analysis shows this to

be a fact. All the salts of silver are formed with it in its univalent condition.

Uses. — Owing to its physical and chemical properties, silver has many important applications in the arts and industries. It alloys readily with many other metals. The alloy with copper is the one most used. The copper imparts its properties to the alloy, making it harder and tougher than the silver alone. It is thus used in coins, in jewelry, table ware, and for many other ornamental purposes. The coin of the United States contains 90 per cent of silver and 10 per cent of copper. English coins contain 92.5 per cent of silver and 7.5 per cent of copper.

Silver is also used to coat various metallic objects, to add to their beauty, and also because it is not acted upon by most of the atmospheric agents. The article to be covered may be made of brass, copper, and alloys like german silver, white metal, etc. The coating may be put on the article by several methods, but by the one most commonly used the silver is deposited by the electric current. It depends on the fact that an electric current decomposes many salts, causing the metal to be deposited on the negative pole of the battery. In this case the salt used is silver cyanid (AgCN) dissolved in potassium cyanid (KCN), forming the compound KCN.AgCN. The article to be coated, or plated, as it is commonly called, is attached to the negative pole of the current and immersed in the bath of silver cyanid; the positive pole is a rod of pure silver, and is also immersed in the silver solution. If the article has a chemically clean surface, the silver is deposited on it in an evenly distributed coating, the thickness of which will depend on the length of time the object remains in the bath, other conditions remaining unchanged. The chemical changes consist, in general, in the decomposition of the silver cyanid into silver and cyanogen, the latter of which, under the influence of the electric current, unites with an equivalent amount of the silver of the positive pole to form silver cyanid again. The action continues, therefore, as long as the positive pole lasts.

Silver is used to form the reflecting surface of mirrors. The silver is deposited on the surface by the action of some reducing agent. This is often done by means of an organic compound called acetic aldehyde. The glass is cleaned and placed in an ammoniacal solution of silver nitrate, the aldehyde is added, and the whole warmed, when the silver is deposited in a thin, brilliant coating on the surface of the glass.

General Methods for the Formation of Metallic Compounds. — Before studying the compounds of silver it is proper to consider the general methods for the formation of metallic compounds, and to notice the classes of compounds that are to be considered. On page 342, Part I., is given a list of the principal classes of compounds that are formed by the non-metallic elements with each other. The metals do not form any stable hydrids, but do form compounds of all the other classes there given, and in addition the class of compounds called salts.

The metallic oxids are produced, in most cases, by exposing the metal to an atmosphere of oxygen, either at ordinary or at raised temperatures, depending on the chemism of oxygen for the element. This method is applicable to all the principal metals excepting silver, gold, and platinum. Or the metal may be oxidized by some oxidizing agent like nitric acid. Other methods will be discussed under the different metals.

Salts, in reference to their formula representation, are formed by the replacement of the hydrogen of acids, either in part or entirely so. Regarding acids as hydroxyl compounds, the changes consist in exchanging the hydrogen of the hydroxyl groups of acids for metals, one unit of valence for another. Silver sulfate, for example, is represented by the formula $\begin{matrix}Ag-O-\\Ag-O-\end{matrix}\!\!\searrow\!\!\nearrow SO_2$. For convenience in writing, it is usual to write this as Ag_2SO_4. The group "SO_4" is characteristic of all sulfates. It is bivalent, as is shown by the two atoms of hydrogen combined with it. Accordingly, this group may be thought of

as an unchanging group present in all sulfates, and as exchanging places with other similar acid groups in chemical actions. In case of any of the oxygen acids, or ternary acids, or their salts, this acid group is always one of the units of exchange, unless oxidation and reduction occur, when the group is broken up into simpler parts, giving up oxygen to some other element or compound; or it may have the capacity to take up more oxygen, and form a more stable compound, at least a more highly oxidized one. What is true of the oxidizing or reducing actions of the ternary acids, as given in Part I. (which see), is true of the salts of these acids, with the general exception that the salts are more stable than the acids and require a higher temperature to produce these changes.

The acids and their salts, under the conditions just stated, that undergo these changes of oxidation or reduction most readily are those that are the least stable, *i.e.* those whose heat of formation is the least. Among these acids and salts are the ternary oxygen acids of nitrogen, the halogens, and the lower acids of phosphorus. These actions, of course, take place when some other compounds are brought in contact with them that readily undergo similar changes. The great majority of the reactions with which we are interested at present are those in which neither of the changes just noted occurs, but those produced by bringing one substance, usually a salt, in contact with another substance (or salt) under the necessary conditions in which some part of one compound exchanges place with a part of the other.

We have already learned what are the conditions necessary for chemical actions, and the methods used in bringing about these conditions. Then it was learned that solution, or that the bodies be in a liquid or a gaseous state, is necessary, in general, for a continuous or complete chemical change, and especially is this true if no other agent than chemism is used to bring about the reaction.

Let us briefly examine what occurs (*a*) when two salts, or an acid and a salt, or a hydroxid, are brought together in solution, and when any compounds that might be formed, by changes in or exchanges among the molecules, are also soluble. For example, suppose that a fairly dilute solution of potassium sulfate (K_2SO_4) is added to a solution of silver nitrate ($AgNO_3$). We may consider that there are four components present in the solution, namely, potassium, the acid group SO_4, silver, and the acid group NO_3; or that there are four affinities acting here, *i.e.* the affinities of potassium for the acid groups SO_4 and NO_3, and those of silver for the same groups. If the affinities were the same for each one of the components, it is readily seen that there would be no change in these two systems, which we may regard as systems in equilibrium.

Since these affinities are not the same, the two systems of equilibrium must be disturbed when the compounds are brought together, and a new system is produced in which there must be four quantities formed; namely, a certain amount of each silver sulfate, silver nitrate, potassium sulfate, and potassium nitrate. The amount of each salt that is produced must depend on the relative affinities of the components for each other, if we consider these factors alone.

Another factor enters into the problem of determining the amount of each substance formed in the case under consideration, and this is the effect that the mass of either of the reacting substances has on the result. That the mass of either of the substances entering into the reaction should change the proportions of the substances is evident, but just how it may act is not definitely determined under all conditions. In some cases, and under conditions when these two factors alone are at work, it has been determined that the proportions of the products depend on both the affinities of the components and the mass of each compound that enters into the change, and

that the latter factor affects the action so that it is proportional to the active mass of each compound that enters into the change. The student must bear in mind that no external force is acting in the case under consideration.

(*b*) The case that is considered here is one in which by a change among the component parts of the two compounds an insoluble substance can be formed. Consider, for example, the reaction when the solutions of the two salts, sodium chlorid (NaCl) and silver nitrate ($AgNO_3$) are brought together. By a change of the bases silver and sodium change places, forming silver chlorid (AgCl), and sodium nitrate, and we may suppose that for an instant of time four compounds exist in equilibrium as given under (*a*); but the silver chlorid, being insoluble, is removed from the sphere of this action, and a new equilibrium is now established. The masses of the constituents have now changed by the removal of the chlorin and the silver, but in the ratio of 107.9 silver to 35.37 of chlorid. A new equilibrium is now established, and is again destroyed by the removal of the molecules of silver chlorid.

The changes go on progressively until all of the chlorin or all of the silver has been removed in the precipitate, silver chlorid. Heat can aid in determining the rapidity of this action.

(*c*) If one of the possible products is a gas in any case similar to that which has been described under (*b*), and the gaseous products can escape, the chemical action becomes complete in a similar manner. This kind of change is illustrated in the production of nitric acid from sodium nitrate and sulfuric acid. When the two compounds are brought together, hydrogen nitrate is one of the compounds formed, and, it being slowly volatile, escapes, but soon the action practically ceases, or proceeds slowly until the temperature of the mixture is raised sufficiently high to volatilize the acid rapidly, when the change goes on until one or the other of the compounds is

exhausted. Several illustrations of this kind of action have already been studied. For example, the production of ammonia from an ammonium salt (NH_4Cl), by the action of calcium hydroxid. The reaction is

$$NH_4Cl + Ca(OH)_2 = CaCl_2 + NH_3 + H_2O.$$

Here when these substances are brought together they mutually react, and calcium unites with chlorin, forming calcium chlorid, setting ammonia free. This is a gas, and escapes. The action, therefore, goes on until one or the other compound has been completely decomposed.

If a large amount of steam is passed over red-hot iron, which has great affinity for oxygen at this temperature, water is decomposed, and an oxid of the metal is formed, and hydrogen is set free. If, on the other hand, this oxid is heated in an atmosphere of hydrogen, *i.e.* in a limited quantity of hydrogen, only a small amount of the oxid is decomposed, water and iron being formed; equilibrium is soon established. If, however, a large amount of hydrogen is passed over the hot oxid, so that the product, water, is carried away, the change goes on until all the oxid is decomposed. This illustrates the effect of mass on chemical action as well as the effect of having one of the products of change a gas under the conditions imposed.

Experimental Study of Silver Compounds, No. 2. — Materials: a soluble salt of silver, the nitrate for example, and solutions of the soluble salts of all the other common acids, and also sodium (or potassium) and ammonium hydroxids.[1]

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[1] The reagents that are commonly on the student's table are solutions of the following salts: $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, KCNS, KCN, K_2CO_3, K_2SO_4, KI, K_2CrO_4, $K_2Cr_2O_7$, $Ba(NO_3)_2$, $AgNO_3$, $CaSO_4$, $MgSO_4$, $HgCl_2$, $(NH_4)_2CO_3$, $(NH_4)Cl$, $(NH_4)_2S_2$, Na_2HPO_4, $Pb(C_2H_3O_2)_2$. Other special reagents should be near at hand; also dry reagents such as sodium carbonate, potassium nitrate, borax, and microcosmic salt, or sodium ammonium hydrogen phosphate ($NaNH_4HPO_4$). H_2S should be prepared as it is needed.

The directions for manipulation are very simple for this and similar studies. In each reaction about 5 to 10 cc. of a dilute solution of silver nitrate is placed in a test-tube, and the reagent is added slowly as long as the reaction continues.[1]

Note the color and appearance of the precipitates and any peculiarities in their formation, *i.e.* any peculiarities that are susceptible of observation. In all cases write the reactions. The student should remember that he is learning the methods of preparing different compounds, the solubility of these compounds, *i.e.* in water, and in cases where it is indicated the solubility in other agents, principally in the acids. A table should be prepared like the one indicated in the appendix.

(*a*) To 10 cc. of the solution of silver nitrate add a solution of sodium chlorid or hydrogen chlorid. The precipitate is silver chlorid (AgCl). What fact does this establish as to the solubility of the compound?[2]

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[1] By a reagent is meant any substance which acting with another substance produces a chemical change. Either substance that enters into the chemical change may be called the reagent. It is customary to apply the term to the substance that is added to another substance. For example, if a solution is placed in a test-tube and a solution of sodium chlorid is added to it, the sodium chlorid is called the reagent. Yet, on the other hand, if it is desired to test for the chlorin of sodium chlorid, the silver nitrate solution is added to that of sodium chlorid, and it becomes the reagent.

Reagents may be classified as general and characteristic. A general reagent is one that produces a reaction with several substances; *e.g.* sulfuric acid sets nearly all acids free from their salts under the proper conditions. A characteristic reagent is a substance that produces a result with a given substance that no other reagent produces, and which it produces with no other substance. The application of these reagents to various substances is called testing or making a test. A test is delicate when a very small quantity of the substance tested for produces visible results. For example, a very small amount of a chlorid in solution (1 part in 100,000 of water) produces a precipitate of silver chlorid with a silver nitrate solution.

[2] Hereafter when the reaction produced is a simple exchange of metals of the compounds, no statement will be made of what the precipitate is, since this would be an unnecessary use of space. However, the learner should

Filter out the precipitate and examine portions of it as follows: To one portion add ammonium hydroxid. The compound formed is $2AgCl.(NH_3)_2$. To this solution add nitric acid until the solution is acid. What is the precipitate? What action would you expect the acid to have on the ammonia? What effect does this produce on the compound? Write the reaction.

To another portion of the precipitate add a solution of sodium thiosulfate; $Na_2S_2O_3.AgNaS_2O_3$ is produced. This fact is used in photography.

To another portion of the solution add slowly potassium cyanid. The compound formed is KCN.AgCN.

(*b*) Add sodium hydroxid to the silver nitrate solution. The precipitate is Ag_2O. Filter out this precipitate and dry it. Transfer to a dry test-tube and, heating carefully, note the changes as the temperature rises. Same for ammonium hydroxid, adding excess. There is formed the compound $AgONH_4$. (In using the alkaline hydroxids, care should be taken in adding them to the solution to be examined. They should be added drop by drop, and finally an excess of the reagent, in each case noting all the peculiarities.)

(*c*) To different portions of the nitrate solution add solutions of the reagents mentioned in the footnote, page 29. Write the reactions and place the result in the table just indicated. Decant off most of the liquid, and add to each tube an excess of nitric acid. Note result.

(*d*) Pass H_2S into a solution of silver nitrate. Note result as before. Pass the gas as long as any precipitate is formed; filter it out and prove whether there is any nitric acid in solution. (See test, Part I., page 255.) Determine whether the acid is free or combined. Is there any silver present in the solution? Test by a soluble chlorid.

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always write out the reaction for the purpose of fixing the formulæ, etc., of the salts. Whenever the reaction is otherwise than this simple exchange of metals, the formula for the compound produced will always be given if it is known.

(*e*) Add to 15 cc. of the silver nitrate solution any one of the following metals, say 2 or 3 g.: Hg, Cu, Sn, Mg, Bi, Pb, and Fe; all these metals produce the same result. Filter out the deposit and determine what it is. Dissolve it in nitric acid and test by (*a*). What is it? Test the filtrate for silver after the metal has been in the solution for 24 hours. Write reactions. Zinc is a bivalent. See (*h*) in Study No. 1.

(*f*) Heat a small crystal of silver nitrate on charcoal. What is the cause of the rapid chemical action? What are the products of the change? Account for all the matter. What part does the charcoal play in the reaction?

(*g*) To the solution of silver nitrate add a solution of $K_2Cr_2O_7$. The normal chromate, Ag_2CrO_4, is precipitated.

(*h*) Pass chlorin into a fairly concentrated solution of silver nitrate as long as any precipitate is formed. Filter out the silver chlorid which is formed, and evaporate the filtrate until all the free chlorin is driven off. Add more water if it is necessary to keep the product in solution, and next add potassium hydroxid to complete precipitation. What is the precipitate? Prove it. Dry and ignite it. Filter out the precipitate, evaporate to dryness, and remove the residue to an ignition tube, and heat to dull redness. What gas escapes? Test with glowing carbon. When the tube has cooled, add water to the residue, filter if necessary, and test for chlorin. Account for the chlorin and oxygen. (See reactions under SILVER NITRATE.)

Compounds of Silver.

(*a*) **Oxids and Hydroxids.** — Under ordinary conditions silver forms but one oxid, Ag_2O. This is according to the valence already established. This oxid is produced by adding potassium hydroxid to any soluble salt of silver, like the nitrate or acetate. The compound produced at first is the hydroxid (AgOH). This compound slowly decomposes

at ordinary temperatures into water and silver oxid (Ag_2O). Heating the suspended precipitate to 60° causes the rapid decomposition of the hydroxid into water and silver oxid (Ag_2O). The hydroxid is quite alkaline, and the oxid when suspended in water imparts an alkaline reaction to it. Heat readily decomposes the oxid into silver and oxygen.

There are two other oxids of silver that have been prepared. They have the formulæ, Ag_2O_2 or (AgO), and Ag_4O, named the peroxid and suboxid of silver respectively. These oxids do not form salts.

(*b*) **Salts of Silver.**— All the acids form salts with silver, the principal ones of which have been studied in the preceding experimental study. The methods there used are commonly employed to produce the insoluble salts of silver. The soluble salts are produced by dissolving the metal, its oxid, or its carbonate, in the acid corresponding to the salt desired. The important salts of silver are those of the halogens and the nitrate.

The halogen salts are all insoluble in water, and are readily produced by treating a solution of any one of the soluble salts with a solution of some halogen salt. Usually those of the alkaline bases are employed. The chlorid is readily dissolved in ammonium hydroxid, while the bromid and iodid are only sparingly soluble, the latter being quite insoluble.

All of the salts of silver undergo chemical change when exposed to light, the change being progressive until the whole of the compound is decomposed and silver is set free. The color changes from the normal color of the salts to purple, and finally to black. The change, in case of the chlorid, is more readily produced than it is with the other two halogen salts. It has been shown that the chlorid loses mass under the influence of light, and that consequently some volatile product is formed. It is probable that a sub-chlorid is formed, Ag_2Cl, and that chlorin escapes from the compound, although some

claim that an oxy-chlorid is the product (see Meldola's *Chemistry of Photography*, page 49), and that no silver is set free.

Photography. — The processes of photography are not properly given in this work, but the chief chemical facts, as far as known, should be studied at this point.

Photography depends chiefly on the facts just stated in reference to the action of light on the halogen salts, although it must not be understood that there are no other salts that are decomposed by light. These facts were well known at the end of the last century, and many illustrations were made of them, but it was not until the year 1845 that photography in anything like its present form was developed.

The chief facts upon which the art rests are: (*a*) The fact of the decomposition of the silver salts by the light; (*b*) that the amount of decomposition depends upon the intensity of the light and the time of exposure; (*c*) that this decomposition can be stopped whenever the operator desires by the use of such an agent as sodium thiosulfate (hyposulfate of sodium), which acts only on the unchanged silver salts; (*d*) and finally after the unchanged salts have been removed, that the decomposition can be completed for the remaining changed salt by means of substances called developers. These developers are substances that are readily oxidized, and consequently reduce the silver to a metallic state. In this finely divided state it is not easily changed, and in the finished photograph it is to a certain extent protected from outside agents.

Silver, finely powdered, is black or dark colored, and thus where the light is most intense there the most silver is deposited, and consequently the darkest tinted. This is true of what is commonly called the negative. The positive picture is produced by making a negative on some transparent medium, and then placing back of this a paper through which one of these silver salts has been evenly distributed. The light passes through the transparent medium and the film, the amount

varying with the density of this finely divided silver (or film). Therefore the effect on the prepared paper will be the opposite of that of the original picture, in the sense that the new picture will be lightest tinted where the negative was darkest or densest. This process is called printing, and much of the art of the photographer is employed in finishing this second picture.

Silver Nitrate. — Silver nitrate is generally made by the action of nitric acid on the metal. The action is the same, in general, as that produced by this acid on metals, which action has been previously described in Part I. It is a process of oxidation and reduction. After the action is complete, the solution is evaporated to dryness to remove the excess of acid. It is then redissolved in water and allowed to crystallize. The salt crystallizes without water of crystallization (see page 111) in colorless, transparent rhombic plates. It is soluble in water and in alcohol.

Silver nitrate is a stable compound at ordinary temperature, but at high temperatures it is decomposed, acting, like nitric acid, as a powerful oxidizer. It is not decomposed by light if pure, but in the presence of most organic matter and other oxidizable substances it is readily decomposed into silver, nitrogen or its oxids, and oxygen, which oxidizes the inorganic matter. These properties suggest the use of silver nitrate for indelible inks. In contact with the organic material, the silver is deposited as a black powder in the fibres of the material and remains adherent to it.

Silver nitrate is also known as lunar caustic, because of its property of oxidizing or destroying animal tissue. When it comes in contact with the skin, for example, it is decomposed, and silver is deposited. The other products act very much as nitric acid does on tissue; *i.e.* it disintegrates and destroys it by oxidation. The name *lunar* was applied to it because of the supposed connection between the moon and silver, and to distinguish the salt from the other caustic substances, such as caustic potash, etc.

Silver nitrate is used as the source of the silver for the halogen salts employed in photography.

When a solution of silver nitrate is treated with free chlorin, it produces a result exactly similar in reference to the silver to that produced when chlorin acts on potassium hydroxid (which see, and (*b*) of last study). The reaction is

$$6\,AgNO_3 + 4\,Cl_2 + 3\,H_2O = 5\,AgCl + AgClO_3 + 6\,HNO_3.$$

Silver Cyanid. — Silver cyanid (AgCN) is another important salt of silver. It is precipitated from the soluble salts of silver by potassium cyanid (KCN). It is soluble in the excess of this reagent, forming the double salt (AgCN.KCN). The solution is the one commonly used in electroplating, as has been previously pointed out.

Silver forms salts with most of the acids, such as silver sulfate, phosphate, etc., the principal facts about which have been learned in the last experimental study.

LEAD (PLUMBUM).

Occurrence and Distribution. — Lead does not occur native except in very small quantities. The principal ore of lead is lead sulfid (PbS). This ore is widely distributed in nature, occurring in crystalline masses, called galena, which is nearly pure sulfid of lead. It also occurs mixed with other sulfids, such as those of silver and copper. In the United States it is found in workable quantities in Illinois, Wisconsin, Iowa, Missouri, in the Lake Superior region, and in the Rocky Mountains.

Preparation. — Most of the lead of commerce is prepared from galena. The process may be divided into two parts: (*a*) in which the ore is roasted, and (*b*) the production of the metal from the roasted mass.

(*a*) By roasting an ore is meant heating it to a high tem-

perature in the presence of air. This is often done by heating the ore in the open air; but more commonly it is heated in a reverberatory furnace through which a strong current of air can be drawn over the heated ore. Under these conditions the oxygen of the air unites with both the lead and the sulfur, forming lead oxid (PbO), sulfur dioxid (SO_2), and lead sulfate ($PbSO_4$). The sulfur dioxid, being a gas, mostly escapes, but some is retained by the lead oxid, which then takes more oxygen, and forms lead sulfate ($PbSO_4$). Portions of the mass that have not come in contact with the air remain unchanged. Therefore, the residue from the roasting process consists of lead sulfid, oxid, and sulfate, providing pure lead sulfid were used. But, as it has been shown, it is rare that the sulfid is found in its pure condition. (Attention will later be directed to such galena as contains silver sulfid as an impurity. When this is present, it is changed during the roasting in much the same manner as is the lead sulfid.)

(*b*) The residue from the roasting is next heated to a high temperature out of contact with the air. Under these conditions the sulfur of the unchanged sulfid unites with the oxygen of the lead oxid and sulfate, setting lead free. The silver compounds undergo similar changes, and it alloys itself with the lead. The amount of silver usually present in galena is very small, yet often it is sufficiently large to modify the good qualities of the lead; at the same time the value of the silver is such as to make it commercially profitable to separate it from the lead.

The facts upon which depends the process for the separation of the silver from the alloys are (*a*) that an alloy has a lower melting-point than that of the metal of the mixture having the highest fusing-point. For example, lead melts at 325°, and silver at about 1000°. An alloy containing a small amount of silver, say 8 to 10 oz. to the ton of alloy, remains liquid after a portion of the lead begins to crystallize out. (*b*) When the richer alloy of silver and lead is heated in the air, the lead

unites with the oxygen, forming the solid oxid, which can be removed, leaving the silver unchanged. The process, as patented by Pattison, in 1833, consists in arranging several large melting-pots in a series, and fusing in the central one a large amount of the silver alloy. It is next allowed to cool until crystals of practically pure lead are formed. These are removed by means of a sieve-like ladle and placed in the pot to the left. The crystals are formed and removed until about three-fourths of the lead has been crystallized. The residue in the central pot is transferred to the pot on the right. Another charge is put in the central pot and melted. The process just given is repeated with each of the pots, and until the last one on each hand is filled. In the right-hand pot is an alloy rich in silver, and on the left there is one filled with nearly pure lead. The process can be carried on until the silver alloy contains about 300 oz. of pure silver to the ton of alloy. The lead is separated from this alloy by the process of cupellation, the essential fact of which is that lead readily oxidizes when heated to a high temperature, while silver is not affected. The lead oxid produced in this process can be heated in a closed crucible with carbon, which removes its oxygen, and thus pure lead is produced. This oxid is known as litharge, or literally, "silver stone."

Parkes' process of separating lead from silver depends on the fact that silver alloys with zinc in preference to lead. Consequently when zinc is added to the molten alloy of lead and silver, the zinc alloys itself with the silver and floats on top of the molten mass and is readily removed. The zinc is removed either by heating the alloy to the temperature of the volatilization of zinc when it escapes, leaving the silver; or by dissolving out the zinc by sulfuric acid, which readily attacks it, but only slightly affects the silver. The more recent process of separating the silver from the zinc alloy is to remove a portion of the zinc by oxidation and distillation, and then cast the remaining

alloy into thin plates. This alloy usually contains silver, gold, copper, and lead. The silver alloy plates are placed in thick muslin bags, which are placed in a bath of dilute nitric acid. These plates are connected with the positive pole of a current of electricity from a dynamo. The negative pole is a plate of pure silver.

The acid dissolves the silver and other metals, except gold, and under the influence of the electric current the compound is decomposed and deposited on the silver pole. The silver thus produced, after being washed, is practically pure. The gold is retained in the bags and is afterwards fused into ingots.

Lead is also produced from its ores by roasting and fusing it in contact with carbon. Again, lead is produced from its sulfid by heating it in contact with iron. The iron unites with the sulfur, and the lead is set free.

Experimental Study of Lead, No. 3. — (*a*) Heat, on charcoal, a compound of lead well mixed with sodium carbonate. Keep it well covered with the carbonate. Let the compound be lead carbonate. What is the first effect of heat on it? What effect does the charcoal have? What is the use of the sodium carbonate? Write the reactions.

(*b*) Heat a piece of lead in air on charcoal — or notice the effect of heating the lead produced in (*a*). Examine by cutting a fresh surface, and gently warming.

(*c*) Place about one gramme of lead tartrate ($PbC_4H_4O_6$) in a narrow test-tube, and heat as long as any fumes escape. Partially close the tube until nearly cool, then cork tightly until cold. When cold, remove the stopper and allow a portion of the contents to fall to the floor from a height of four or five feet. Note and explain the result. Remove some of the material and treat it with nitric acid. What remains? Prove that the solution contains lead (see page 43, for tests). In what condition is the lead after the decomposition of the tartrate? Is this lead more readily attacked by oxygen than

ordinary lead? Why? Account for the changes in the tube when the tartrate is heated.

(*d*) Treat small pieces of lead (or, better, granulated lead) with the three acids, HNO_3, HCl, H_2SO_4, and observe the action of each acid at ordinary and higher temperatures, and explain and describe each case. Which is the best solvent? In case of nitric acid, concentrate the solution and allow the lead nitrate to crystallize. What were the brown fumes that escaped? Write the reaction. Use acetic acid in the same way. Leave the lead standing in the acid for some time.

(*e*) Heat some lead powder with sulfur, and examine the product.

(*f*) Heat fine lead powder in chlorin water. Explain.

(*g*) Grind fine powdered lead and iodin in a mortar with a little water or alcohol. Does the iodin unite with the lead? Explain.

Physical Properties. — Lead is a soft metal of a bluish color. It is so soft that it is easily rubbed off when passed over paper, leaving a grayish black mark of finely divided lead. It is one of the heavy metals, having a specific gravity of 11.3 The metal is quite malleable and ductile. It fuses at 325°, and is converted into vapor at about 1700°. It is not very tenacious, since a wire 2 mm. thick has a tensile strength of less than 10 kg.

Chemical Properties. — Lead readily unites with oxygen at high temperatures, and slowly at ordinary temperatures. At ordinary temperatures the oxid forms a coating over the surface of the lead and prevents further oxidation. If lead is in a very finely divided condition, it oxidizes so rapidly in the air that it raises the mass to red heat, as was seen in the study of lead tartrate. Lead is not attacked at ordinary temperatures by either sulfuric or hydrochloric acids, and at high temperatures even the action is only slight. The products of the action of sulfuric acid at boiling temperatures are the usual ones when

this acid acts on metals under these conditions; namely, sulfur dioxid, a sulfate, and water. Nitric acid readily dissolves lead, forming the nitrate and the other usual products. It is dissolved by acetic acid quite readily, and especially so if the lead is in contact with air. This action is true of many weak acids. The lead in contact with the air becomes coated with a thin layer of lead oxid, which the acid readily dissolves. The oxid is again formed and dissolved, the action being repeated as long as either agent lasts.

Zinc and other metals precipitate lead from solutions of its salts in the form of crystals, the "arbor Saturni" of the alchemists. It unites with sulfur and the halogens at raised temperatures, forming the corresponding binary compounds.

Atomic Mass and Valence. — Lead forms several compounds that have been converted into gases. One of these is lead chlorid, and the other is a compound of lead with carbon and hydrogen called lead tetra-methid. The vapor density of the chlorid is 138.57, and its molecular mass accordingly is 277.14. Quantitative analysis shows that 74.47 per cent is lead, and 25.53 per cent is chlorin. These per cents of the molecular mass give 206.4 parts of lead and 70.74 parts of chlorin. This amount of chlorin corresponds to two atoms. Hence the 206.4 parts of lead correspond to two atoms of hydrogen. Thus lead has a valence of two, or it is a bivalent.

The other compound just mentioned has a vapor density of 133.2, and contains 77.47 per cent of lead, 18.01 per cent of carbon, and 4.52 per cent of hydrogen. The molecular mass contains 206.4 parts of lead, 48 parts of carbon, and 12 units of hydrogen. (Show how this is.) Again, it is found that 206.4 corresponds to 32 parts of sulfur and 64 parts of oxygen. This number, 206.4, is taken as the atomic mass of lead; it is certainly the combining mass of the element. It is the smallest amount found in any gaseous molecule, and it is the amount

that is found in other molecules when the usual atomic proportions of the other elements are used.

Lead is bivalent in all of its salts, since 206.4 parts (or one atom) replace two atoms of hydrogen.

Uses of Lead. — The softness, flexibility, and malleability of lead determine its use for many purposes. In the form of tubes it is used to convey liquids, and in the form of sheets to cover roofs, and other similar purposes. The fact that it resists the action of many substances, and the comparatively slight action of the air upon it, leads to its use in a great variety of ways. This is illustrated by its use for the vessels in which sulfuric acid is prepared. Its application as pipes in which to convey water, used for drinking-purposes, should be avoided, since it is likely to be attacked by the impurities in the water-forming compounds that are either soluble or are left in a finely divided state suspended in the water, and being usually white compounds, are not easily seen. Some of these impurities that are often in waters used for drinking-purposes are organic matter, nitrates, and nitrites. The compounds of lead are poisonous, and when taken into the system in small quantities produce cumulative poisoning.

Lead alloys readily with many of the metals, forming useful substances such as solder, shot, type-metal, etc.

Ordinary shot are an alloy of lead and arsenic, containing about 2 per cent of the latter. The arsenic is said to cause the shot to be spherical when they are made in the usual manner. If no arsenic is used, the shot are elongated, or pear-shaped, and if too much arsenic is used, they become flattened. Solder is an alloy of tin and lead. The most fusible alloy contains about 40 per cent of tin and 60 parts of lead. This fuses at 184°. Equal parts of lead and tin fuse at 186°. Tin alone fuses at 228°. In type-metal is sought a fusible substance that can be cast into type, and the same time one that is not too soft nor too brittle. An alloy of 1 part of antimony and

4 parts of lead furnishes a metal that is quite hard and not brittle, and yet is readily fusible and expands slightly on cooling, — facts necessary to good type-metal.

History and Name. — This metal was one of the seven elements that have been known from early times. Each of these seven elements was connected with some one of the then known planets. Lead was most appropriately connected with Saturn because of its dull color, when contrasted with silver and gold. The metal was called plumbum by the early Romans. The same idea is used in the expression "plumb-bob," *i.e.* a heavy body. The metal was obtained in large quantities by the Romans from the mines of Spain and England. The symbol, Pb, is derived from the word *plumbum*, although its common name *lead* is of Anglo-Saxon origin.

Experimental Study of the Compounds of Lead, No. 4. — (*a*) Heat a globule of lead on charcoal, and note the color of the oxid that is formed when hot and when cold. Cover it well with sodium carbonate and fuse the mass. Explain the result.

(*b*) Place in a crucible a gramme of lead oxid (PbO) and heat it to about 300°. Note the change in color. What produced the change? Treat a little of the substance with nitric acid. Also a little of the original oxid. The brown powder is lead dioxid (PbO_2). From whence is the oxygen?

(*c*) To a gramme of lead oxid (PbO) add dilute nitric acid warm, adding more acid if necessary to complete the solution. Write the reaction. Evaporate the solution until the solid lead nitrate begins to form. Allow the solution to stand until the salt crystallizes. Remove one of the crystals, and heat it to redness in a tube. What is left in the tube? What escapes? What does this say about the stability of the nitrate? What is its solubility? Add water to a dry crystal and attempt to dissolve it. Is a new compound formed? With what? Now add a few drops of nitric acid, and warm if necessary to dissolve the precipitate.

(*d*) **Heat** for some time .5 g. of lead oxid in 25 cc. of pure water. Test the water with red litmus paper. Turn off 10 cc. of the water and pass into it hydrogen sulfid. What is indicated by the result?

(*e*) To 10 cc. of the solution of lead nitrate add hydrochloric acid as long as any precipitate is formed. Allow the precipitate to settle, pour off the liquid, add 10 cc. of water, and boil. Add more water, and boil if the compound does not all go in solution. Run cold water on the test-tube and note what happens. Note solubility. Suppose this chlorid were mixed with silver chlorid, how would treating the mixture with much boiling-hot water affect them? How could you make lead chlorid from metallic lead?

(*f*) To other portions of the solution of the acetate add H_2SO_4, KI, $(NH_4)_2S_2$, $(NH_4)_2CO_3$, K_2CrO_4 (or $K_2Cr_2O_7$), Na_2HPO_4, etc. Write the reaction in each case. Filter and wash the sulfid, and treat with nitric acid. Same for the carbonate. Write the reactions. What is the source of the free sulfur? Every negative element when made positive must pass through what condition?

(*g*) To the same solution add Na_2CO_3. There is formed $PbCO_3$, $Pb(OH)_2$. This precipitate has a somewhat variable composition.

(*h*) To the same solution add NaOH. The precipitate is $Pb_2O(OH)_2$, or basic hydroxid. (See BASIC COMPOUNDS, page 64.)

(*i*) Place a stick of zinc in 20 cc. of a concentrated solution of lead acetate acidified with a little acetic acid. The action is hastened by placing in the solution a piece of platinum foil so that it touches the zinc. Let the solution stand for several hours. Remove the deposit by filtering, wash, dry, and fuse in a porcelain crucible, covering the residue with sodium carbonate. What changes have been produced?

(*j*) Add to 20 cc. of a boiling solution of lead acetate,

finely powdered lead oxid (PbO) as long as it dissolves. Filter and pass CO_2 into the solution. Lead carbonate is produced. Let the solution stand in the air. Account for the film that forms on top of it. (See (*f*).)

(*k*) Heat a gramme or more of lead carbonate to dull red heat. Note the changes in color and any volatile substances that appear. What are the products?

(*l*) Place lead dioxid (PbO_2) in a tube (calcium chlorid tube, straight or U shaped), and pass over it dry sulfur dioxid. Note changes of color. Compare with the result when a soluble salt of lead is treated with a sulfate. Also add the dioxid to a solution of sodium sulfate. (Neutral and alkaline solution.) Note differences.

(*m*) Filter out the lead sulfate of (*b*) and add to a portion of it alkaline ammonium tartrate or acetate. Warm. To another portion add sodium hydroxid and heat. Compare with barium sulfate as to solubility in same media.

Compounds of Lead.

(*a*) **Lead and Oxygen.** — When lead reacts with oxygen at high temperatures, it forms but one compound, and that, according to the valence just determined for the element, has the formula PbO. When this oxid is treated with nitric acid, lead nitrate is formed, from which other salts are readily produced. This is the only oxid that forms salts.

There are three other oxids of lead that have been prepared under different conditions. They are quite stable compounds, but when treated with acids produce salts corresponding to Pb″. These are represented by the formulæ Pb_2O, lead suboxid; PbO_2, lead dioxid; Pb_2O_3, lead trioxid.

Lead dioxid is an oxidizing agent, every molecule yielding one atom of oxygen and one molecule of lead oxid (PbO). The dioxid is a more active oxidizer in the presence of alkalies. It

rapidly oxidizes sulfur dioxid, forming lead sulfate, producing a large amount of heat as a result of the reaction. Sulfuric acid decomposes it by the aid of heat, setting oxygen free and forming lead sulfate. Hydrogen chlorid is decomposed by it in a manner similar to its decomposition by manganese dioxid (MnO_2) when it is used to prepare chlorin. Write the reaction. It is formed from red lead or minim (Pb_3O_4) triplumbic tetroxid, by the action of nitric acid. Red lead has been found to consist of two molecules of PbO and one molecule of PbO_2, $2\,PbO.PbO_2$. Minim is used as a pigment in painting, in making cement, and in the production of flint glass (which see).

The reaction with nitric acid is as follows: —

$$(PbO)_2PbO_2 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + PbO_2 + 2\,H_2O.$$

Both minim and lead dioxid are decomposed at high heat into oxygen and lead monoxid, illustrating again the effect of heat on chemism. Minim is formed by heating lead oxid (PbO) to temperatures between 300° and 340°. At temperatures near red heat the decomposition takes place. In the case of the lead dioxid the metal is a tetrad. When this oxid is dissolved in potassium hydroxid, a compound is formed in which lead appears to act with acid properties. It is represented by the formula K_2PbO_3, or $O = Pb\begin{smallmatrix}/O-K\\\backslash O-K\end{smallmatrix}$. Lead oxid (PbO) is commonly called litharge (silver stone) and sometimes massicot.

(*b*) **Lead Hydroxid.** — Normal lead hydroxid is probably not produced; but the basic hydroxid ($Pb_2O(OH)_2$) is formed by treating a solution of a salt of lead with potassium or sodium hydroxid. It readily takes up carbon dioxid even from the air, forming a basic carbonate. It is soluble in excess of the reagent, producing potassium plumbite (K_2PbO_2). The basic character of the compound is shown by the formula of the molecule which is represented thus, $\begin{smallmatrix}OH-Pb\backslash\\OH-Pb/\end{smallmatrix}O$.

(*c*) **Salts of Lead.** — Lead, like silver, forms salts with all of the principal acids. Many of its salts are basic, especially those salts formed with the weak acids. Lead forms but few soluble salts, as has been shown in the experimental study. The soluble salts are the nitrate, acetate, and chlorate. The principal salts of lead are the nitrate, acetate, the sulfid, halogen salts, chromate, and carbonate.

Lead Nitrate. — Lead nitrate, being soluble, cannot be produced by precipitation, but is produced by the action of nitric acid on lead, lead oxid (PbO), or lead carbonate. The solution is evaporated to crystallization, when anhydrous crystals separate out. When heated alone, the nitrate readily breaks up into lead oxid (PbO), and chiefly nitrogen dioxid (NO_2), and oxygen. Lead forms a basic nitrate of the formula, $NO_3-Pb-OH$. It is produced by boiling a solution of the nitrate with lead oxid.

Lead Acetate. — This compound, a salt of an organic acid, is produced by the action of acetic acid on lead in presence of air or by its action on lead oxid (PbO), or carbonate. By the first action basic salts are generally produced. The normal salt ($Pb(C_2H_3O_2)_2$), is very soluble in water, from which it crystallizes with three molecules of water. The substance is called "sugar of lead" because of its sweetish taste. It was so named by Valentine because he found that when lead oxid was boiled with vinegar, the acid property of the latter was destroyed and a sweetish product was formed, which he compared in general appearance and taste to sugar. When the normal salt is heated above 100°, it is partially decomposed, and some acetic acid is driven off, and there is left a basic salt. Basic salts are also made by boiling lead oxid in a solution of normal lead acetate. There are two such salts known. They are represented by the formulæ —

$$Pb_2O(C_2H_3O_2)_2 \text{ and } Pb_3O_2(C_2H_3O_2)_2,$$

and are known as di- and tri-basic sub-acetates, or di-plumbic-oxy-diacetate and tri-plumbic-di-oxy-diacetate respectively. The solutions of these sub-acetates are very sensitive to the presence of carbon dioxid, absorbing it and forming lead carbonate. These salts have many uses in medicine and the arts. The normal acetate is used to prepare chrome yellow, lead chromate ($PbCrO_4$), lead iodid (PbI_2), and other pigments. It is used in medicine, but in large doses is a powerful poison.

Lead Carbonate. — Lead carbonate occurs in nature and is known as cerusite. This mineral occurs in relatively small quantities only, and is commercially prepared by the action of carbon dioxid on basic lead acetate. The carbonate is insoluble in water, and consequently can be formed by precipitation by using some one of the three soluble carbonates. Ammonium carbonate precipitates the normal carbonate, but sodium or potassium carbonate precipitates the basic salts.

The lead carbonate, known as white lead, is a basic carbonate of varying composition, the variability depending on the method of manufacture. The oldest method of commercial manufacture is based (*a*) on the action of acetic acid on metallic lead in the presence of air and moisture, and (*b*) on the action of carbon dioxid on the product of the first action. In (*a*) the lead is converted into basic lead acetate of variable composition, depending on the conditions under which it is prepared. It may be represented by the formula $Pb_3O_2(C_2H_3O_2)_2$. The second reaction produces basic lead carbonate, $Pb_3(OH)_2(CO_3)_2$.

$$Pb_3O_2(C_2H_3O_2)_2 + 2\,CO_2 + 2\,H_2O = Pb_3(OH)_2 \cdot (CO_3)_2 + 2\,HC_2H_3O_2.$$

The method referred to is called the Dutch process. By this method metallic lead is exposed to the vapors of acetic acid, carbon dioxid, and moisture. The heat necessary to vaporize the acid and heat the sheets of lead is produced by

the chemical changes that go on in decaying stable refuse or other decomposing organic matter. Carbon dioxid, one of the products of this decomposition, and moisture are always present under the conditions. It is seen by the reaction given that the acetic acid is set free again, which is thus ready to unite with more lead. This action goes on until the sheets of lead become thickly coated with the carbonate, when they are taken from their covering of manure, and it is removed by gently striking them. If the lead sheets are not entirely destroyed, they are placed again under the conditions just described.

More recent methods for the manufacture of white lead exchange the slow process of the formation of basic lead acetate employed in the Dutch method for the simple one of heating the neutral acetate with lead oxid (PbO), and when the carbon dioxid has converted this into the insoluble carbonate, the solution is heated with more lead oxid. (See (*h*).) By the proper arrangement of apparatus this process can be made continuous and rapid.

When this pigment is washed and dried to remove adherent impurities, it is ground to a very fine powder and mixed with oil. It constitutes the ground white lead paint of commerce. An objection to its use is found in the fact that it often turns black, and especially is this true in cities where the atmosphere contains small amounts of hydrogen sulfid. This forms, with the lead of the carbonate, lead sulfid. Other substances are often used in place of the white lead. (See under ZINC and BARIUM.)

The Halogen Salts. — The halogen salts are generally produced by the method given in the experimental study, *i.e.* by treating a soluble salt of lead (acetate or nitrate) with a soluble halogen salt. It can also be prepared by the action of hydrochloric acid on the carbonate or oxid. The chlorid is of importance principally in analytical chemistry. It is quite

soluble in boiling hot water, — 1 g. of the chlorid to 30 g. of water. Cold water dissolves 1 g. in about 150 g. of water. It is insoluble in ammonia, but forms with it an insoluble basic chlorid. These two facts are made use of in separating and recognizing soluble silver compounds in the presence of soluble lead compounds. A characteristic of the lead chlorid is the rapid formation of crystals when its hot, saturated solution cools down to ordinary temperatures.

Lead iodid and bromid are prepared in a manner similar to that used for the formation of the chlorid. They are less soluble than the chlorid, but behave very much like it when their hot, saturated solutions cool down to usual temperatures. The iodid deposits beautiful yellow, glistening crystals of the normal iodid.

Lead Chromate. — Lead chromate is a beautiful yellow salt used as a pigment in painting. Its production from a soluble salt of lead and the normal potassium chromate is quite characteristic.

Other Salts. — The sulfate and sulfid are both insoluble salts of this metal, and both are found in nature, the latter being the usual source of the metal. The sulfate is soluble in basic ammonium tartrate or acetate; also in sodium hydroxid. These facts serve to distinguish it from the insoluble barium sulfate. All the salts of lead are decomposed by hydrogen sulfid, forming the sulfid. The sulfid is soluble in nitric acid, but is very insoluble in water, so much so that a solution containing one part of lead in 100,000 parts of water is blackened by passing hydrogen sulfid through it.

Lead salts are all poisonous, producing both acute and chronic poisoning. Attention has been called to the action of impure water on the metal when used to line cisterns or tanks. If the water contain carbonates and sulfates, the vessels soon become coated with these insoluble compounds, and thus protect the lead from further corrosion. However, the carbonate

may be removed by mechanical means from the walls of lead pipes, and if water conveyed in these pipes is used for drinking-purposes, that compound is dissolved in the stomach and is absorbed into the system. The lead compound thus taken into the system is very slowly eliminated, and in course of time very disastrous effects are produced. Persons employed to handle or manufacture lead compounds are often slowly poisoned. Acute lead poisoning produces symptoms similar to those of antimony, *i.e.* violent pain and great irritation in the alimentary canal. Death follows quickly after the poison is swallowed. The antidote is magnesium sulfate in solution, or any soluble sulfate that is not itself poisonous. The principal action of the antidote has been shown in the experimental study under (*c*).

MERCURY.

Occurrence and Distribution. — Mercury is not widely distributed, it being found in only a few localities. The principal ones are in Spain, Japan, Russia, and California. In these localities it occurs in both the free and combined condition. Its principal compound is mercury sulfid (HgS), commonly called cinnabar, the Latin name of the ore. The native mercury occurs in minute drops in the cinnabar ore.

Preparation. — The metal mercury is almost exclusively prepared from the native sulfid. The separation of the sulfur from the mercury is very easily accomplished, since the affinity between the two elements is very small at raised temperatures.

The ore is broken up and roasted either alone or with iron. In the former case the sulfur is oxidized to the dioxid, and the metal is converted into a vapor which escapes along with the dioxid. The mercury readily condenses on the cool parts of the apparatus used and is easily removed. If iron is heated with the sulfid, sulfid of iron is formed, and mercury is vaporized

as before. In a few localities the ore occurs along with limestone, calcium carbonate ($CaCO_3$). Here the ore is broken up and placed in iron retorts and heated until the mercury distils over. The reaction that occurs is —

$$4\,CaCO_3 + 4\,HgS = 4\,Hg + 3\,CaS + CaSO_4 + 4\,CO_2.$$

Mercury thus obtained contains impurities, both mechanical and alloyed. It is redistilled, which removes mechanical impurities and some of the alloyed metals. It is often treated with dilute sulfuric and nitric acids, which remove such alloyed metals as lead, tin, and zinc. It is finally purified by redistillation.

Experimental Study, No. 5. — Recall and bring together the studies given in Part I. in which mercury is used.

(*a*) Weigh a cubic centimetre of mercury and determine its specific gravity.

(*b*) Heat a globule as large as a pea in a narrow test-tube, and, if it is possible, determine the temperature at which it rapidly vaporizes.

(*c*) Heat a globule of mercury in the air to about its boiling-point. What is the solid substance? Of what must it be composed?

(*d*) Brighten a strip of copper and rub a little mercury over it. Attempt to rub it off. Place mercury on a tarnished piece of copper. Note result. What is sodium amalgam? Where has it been used?

(*e*) Weigh out 2 g. of mercury and 1.26 g. of iodin, place them in a mortar, and rub them together, adding a little alcohol. Note the color. What is formed? Rub until all the mercury disappears. Is there any of either element free?

(*f*) Proceed as in (*e*), except that the quantity of iodin is doubled, or add as much more iodin to (*e*), and rub it in the mortar as before. Note the color. How do these compounds differ in quantitative composition? In what two proportions

do mercury and iodin unite? Suppose you used a greater amount of either element than is here given, what would have resulted?

(*g*) To a gramme of mercury add 25 cc. of dilute nitric acid (10 per cent solution), allow the acid to act at ordinary temperatures, and continue the action until the mercury dissolves, adding more acid if necessary to complete the solution. What gas escapes? How does nitric acid act on metals? Save the solution for further examination under the next study.

(*h*) Use the same amount of mercury with concentrated acid, using heat to complete the solution. Boil for some time, and save the solution as in (*g*).

(*i*) Test the solubility of the mercury in hydrochloric acid and in concentrated sulfuric acid. Use heat in each case. What gas escapes in the case of sulfuric acid? Save this solution for further examination.

(*j*) Put a globule of mercury in 10 cc. of a silver nitrate solution acidified with a drop of nitric acid. Allow this to stand undisturbed for several days. Then turn off the clear solution and test it for mercury, according to the next study. Test it for silver, provided that there is an excess of mercury.

(*k*) Place a globule of mercury in a bulb-tube and pass over it chlorin gas. Warm the bulb. Note the result. Remove the product and heat with water, and add potassium iodid to the solution. Explain after making the next study.

Physical Properties. — Mercury is the only metal that is liquid at ordinary temperatures. It is a solid at $-39°.5$. It behaves like an ordinary liquid under the influence of heat, *i.e.* it is slowly vaporized as the temperature is raised, but at $357°.5$ its temperature becomes stationary and it is rapidly vaporized. It is one of the heavy metals, its specific gravity being 13.596 at ordinary temperature and 14.39 at $-40°$. Its vapor density is 99.9.

Chemical Properties. — Mercury is not acted upon by air at

ordinary temperatures, but at about 360° it unites with oxygen, forming the red mercury oxid (HgO). It is quite readily attacked by ozone. It unites with sulfur and the halogens even at ordinary temperatures, forming the corresponding binary compounds. In case of the halogens, as has been seen, there are two compounds formed in each case, one containing twice as much of the halogen as the other. Mercury is not acted upon by hydrochloric acid at any temperature, nor by sulfuric acid at ordinary temperatures. At high temperatures it is dissolved by sulfuric acid, forming the usual products when hot sulfuric acid acts on metals; *i.e.* sulfur dioxid, water, and the oxid of the metal, which, in this case, is converted into the sulfate. Nitric acid readily dissolves mercury even in the cold, producing the usual product with nitric acid and a metal. (See under COMPOUNDS OF MERCURY.)

Mercury is an active poison when taken into the animal body, especially when its vapor is inhaled. It produces salivation with the usual accompanying disorders of the body.

Atomic Mass and Valence. — The vapor density of mercury is 100 (99.9). This number, therefore, bears some simple numerical relation to its atomic mass. In case of most of the elements studied, the vapor density and the atomic mass have been identical, but an examination of the compounds of this element leads to the conclusion that its atomic mass is 200 (199.8). Mercury forms several volatile compounds, but those formed with chlorin are the best known. As has already been shown, there are two of these compounds, one having twice as much chlorin as the other. The one containing the least chlorin has a vapor density of 117.58. It contains 84.92 per cent of mercury and 15.01 per cent of chlorin. Therefore, the molecule contains 199.8 units of mercury and 35.37 units of chlorin. The vapor density of the compound containing the more chlorin is 270.54. A similar analysis shows that this molecule contains 199.8 units of mercury and 70.74 parts of

chlorin. This is the smallest amount of mercury found in any gaseous molecule containing it, and is the unit amount that enters into all chemical changes. It is, therefore, the atomic mass and combining equivalent of mercury. It appears from the facts just given that mercury is capable of combining with one or two atoms of chlorin, and therefore that it is both univalent and bivalent. An examination of the other salts of the element shows that it can replace one or two atoms of hydrogen.

The formulæ, therefore, for these chlorids are HgCl and $HgCl_2$. There is some evidence pointing to the formula Hg_2Cl_2 for the first of these compounds; but since the first formula, HgCl, agrees with its vapor density and percentage composition, and the other facts to the contrary are not yet wholly understood, it is considered best to use the first formula, HgCl. These two classes of compounds are distinguished by applying the suffixes "ous" and "ic" to the name of the metal. They are called, therefore, mercurous and mercuric chlorid respectively. The two classes of compounds can be readily changed from one form to the other by the proper oxidizing or reducing agents.

Name and History. — Mercury is included among the first known elements, the names of which were connected with the planets known to the ancients. The early chemists often applied the name *mercury* to substances that were volatile. This element was thought by the alchemists to form a part of other elements. Later it was much studied because of its supposed medicinal properties. The effects of this study are shown by the number of compounds and preparations that are yet used in medicine. The symbol Hg is derived from the word *hydrargyrum*, which is formed from the Greek words for water and silver. This was translated into *argentum vivum* by the Latin writers, and later into *quicksilver* by the English-speaking chemists.

Uses. — Mercury alloys itself readily with nearly all of the

metals, forming combinations that are called amalgams. These amalgams are liquid or solid, depending on the amount of mercury used. In case of some of the metals the combination is formed with the production of light and much heat. This is especially true of its alloys with sodium and potassium. They are solid if the amount of the alkali metals is more than 3 per cent. These solid amalgams with the fixed alkalis have been prepared that contain atomic proportions. They are crystalline compounds having the formulæ $HgNa_2$ and HgK_2. The amalgam with tin (which see) is used for making the reflecting surface of mirrors. Mercury has many uses that grow out of its fluidity and general chemical inertness at ordinary temperatures, such as its uses in barometers and for many kinds of apparatus that are used for collecting and measuring gases.

This property of readily amalgamating with other metals is made use of often in separating gold and silver from their ores. The mercury being volatile, it is removed from the metals by heat, and then condensed for further use. In medicine it is used in a finely divided form mixed with several substances, most of which are in themselves inert. For example, pure calcium carbonate or chalk and mercury are rubbed together in a mortar until the mercury becomes invisible as distinct globules. It is also rubbed up with fats, such as lard, and used as an ointment. Blue mass is another common preparation, composed of powdered licorice root and mercury ground together. In all these preparations containing metallic mercury, it is probable that the effect is due to the small amount of mercury oxid that is formed by the oxygen of the air in contact with the finely powdered mercury.

Compounds of Mercury.

General Statement. — As has just been stated, mercury forms two classes of compounds; *i.e.* with the same acid there

may be produced two compounds or normal salts of mercury, but one always contains twice as much of this element as the other for the same amount of the acid group. These compounds are quite distinct in nearly all their physical and chemical properties. The two classes of salts are readily changed from one form to the other by oxidizing or by reducing agents. Solutions of mercurous compounds are oxidized even by standing in the air. This most readily occurs when there is some acid present. This change is prevented by adding a little free mercury to the solution.

Experimental Study of Mercury Compounds, No. 6. —(Use the solutions prepared in (*f*) and (*g*), Study No. 5, and if more of the solution is needed, it should be furnished the student ready prepared.)

(*a*) To 5 cc. of the solution (*f*) add hydrochloric acid as long as any precipitate is produced. Give the same treatment to solution (*g*). Explain the difference in the two cases.

(*b*) Compare the action of the usual reagents on these two solutions (always use small amount, and follow by excess). Write the reactions where precipitates are produced, and place the results in the proper table. The fixed alkalis form the corresponding oxids of mercury. Ammonium hydroxid produces compounds of the form of $(NH_2Hg_2)X$ for mercurous salts, and $(NH_2Hg)X$ for mercuric salts, "X" representing an univalent acid group. Soluble carbonates form the normal carbonate with the soluble mercurous compound in the cold. This changes to basic carbonate and the oxid when heated. The mercuric compounds, under the same conditions, form the basic carbonate, $3HgO.HgCO_3$. Heat decomposes this carbonate into the normal oxid, HgO.

Note particularly the reaction with H_2S and $(NH_4)_2S$. Treat the mercuric sulfid with nitric acid, and boil. Next add a few drops of hydrochloric acid. Take another portion of the black sulfid and warm it in ammonium sulfid. Dry another portion and transfer it to a dry tube and sublime it.

(*c*) Heat a little dry mercuric chlorid with sodium carbonate in a test-tube. What are the deposits on the tube? What part does the sodium carbonate play in this action? Heat the tube to dull red heat until the change is complete. Next allow it to cool, remove the substance left in the bottom of the tube, dissolve it in water, and test for hydrogen chlorid. What does this show? Write the reactions.

(*d*) Place a bright strip of copper in a solution of mercuric chlorid. Explain the action. Compare with silver and mercury, noting the difference in the electrical relation.

(*e*) To a solution of mercurous nitrate add nitric acid, and boil. Note any fumes that escape. What are they? Prove whether any change has occurred. Drive off the excess of acid, and test portions of the solution with KI and KOH. What does this prove? Write the reactions.

(*f*) To a solution of $HgCl_2$ add, drop by drop, a solution of stannous chlorid. What is the white precipitate at first formed? Add excess of the tin chlorid, warm to boiling temperature, and filter out the precipitate. Rub the gray residue with some hard body. What is the result? Explain what has occurred so far as the mercury compound is concerned. Where is its chlorin? Test for it. Where is the tin? See under TIN, for tests.

(*g*) Try to dissolve a crystal of mercurous nitrate in 10 cc. of water. Filter, and test the filtrate with KI. Wash the residue on the filter-paper into a test-tube, and add nitric acid, and warm. Nearly neutralize the solution with ammonium hydroxid, and test as before. The first precipitate has the formula $Hg.NO_3.HgOH$. Explain how this compound is produced under the conditions. What substances were present? Explain the action throughout. How can you distinguish the two classes of mercury salts?

(*h*) Heat a crystal of mercury nitrate in a test-tube nearly to redness. Note escaping substances. What is left in the

tube? Suppose the heat had been bright red heat, and it had continued for some time, what would have been the result?

(*i*) Treat the precipitated mercurous chlorid of (*b*), after it has been washed and filtered, with ammonium hydroxid. Compare this action with that of this reagent on silver chlorid or on lead chlorid. This action is characteristic of mercurous chlorid, and serves to distinguish it from both silver and lead chlorids.

(*j*) Filter out and wash the mercuric sulfid produced in (*b*), and treat it with hot nitric acid. Next add a little hydrochloric acid to the mixture. (Sulfur is set free by this action, and can be readily distinguished from the undissolved sulfid by the fact that it floats on the surface of the liquid, and can be readily removed.) Evaporate the solution to dryness, and redissolve the residue. Treat a portion of the solution with KI, and another portion with stannous chlorid. Filter out the precipitate of mercuric iodid, allow it to dry on the paper, and note the effect of pressure and rubbing on its color. Warm some of it. This action is quite characteristic.

(*k*) Add a solution of mercuric chlorid to the solution of the white of an egg. Shake well. The white-of-egg solution is made by shaking the "white" with four or five times its volume of water.

Hydroxids and Oxids of Mercury. — According to the valence of mercury there should be two oxids, having the formulæ Hg_2O and HgO. These oxids are known, although it is doubtful whether the lowest oxid, Hg_2O, has been produced in a pure condition. It is said to be formed when any soluble mercurous salt is acted upon by a fixed alkali. The precipitate is black, and gradually changes, on standing, into free mercury and mercuric oxid. However, when it is dissolved in acids, mercurous salts are formed. The oxid is decomposed quite readily by heat or light into mercury and mercuric oxid.

Mercuric oxid (HgO) is produced by heating mercury to

about 360° in the presence of oxygen, when the red oxid is formed on its surface. This was the method used by the immortal Lavoisier when he showed that the air was composed of two gases, one of which he named oxygen. The oxid prepared in this manner is a red crystalline substance, and is much more resistant to the action of reagents than is the yellow amorphous oxid. For example, chlorin reacts but slightly with the crystalline variety, while the yellow oxid under the same conditions is decomposed, and hypochlorous oxid is formed. The yellow oxid has exactly the same proportions of the elements mercury and oxygen, but it is produced by the action of the fixed alkalis on soluble mercuric salts. The crystalline oxid can be converted into yellow oxid by mechanical means, such as rubbing in a mortar. These differences of color are due apparently to physical causes. Heat produces change of color from red to black, but when the oxid cools, it resumes its original color. This oxid is also produced by heating its corresponding nitrate or carbonate. It is soluble in acids according to the usual reaction between acid and metallic oxids. The hydroxids of mercury have not been prepared.

Salts of Mercury. — (*a*) **Halogen Salts.** — The halogens all unite directly with mercury, either by rubbing them together, as in the case of bromin and iodin, or by slightly heating the mercury in contact with these elements in the form of gases. They are also produced by the action of soluble salts of these elements, or the solution of their hydrogen compounds on the soluble salts of mercury (-ic and -ous), with the exception of mercuric chlorid, which is soluble in water. The normal salts are formed in each case. The iodids possess the same property as the oxids, that of changing color under different conditions. This is especially true of the mercuric iodid (HgI_2). Mercurous iodid is a greenish yellow substance. It is an unstable compound, changing readily to mercury and mercuric iodid.

The most important of the halogen compounds are the two chlorids. They have been used from early times in medicine under the names of calomel and corrosive sublimate. The word *calomel* signifies a "fine black," and probably refers to its method of production. It was prepared by heating a mixture of mercury and corrosive sublimate (which was black), and driving off the white calomel or mercurous chlorid in the form of a vapor. It can be produced by any of the general methods just given for the halogen salts. It is a very insoluble amorphous substance, and was much used in the earlier times by the medical practitioners, and is to some extent yet. It is a poison, but acts slowly because of its insolubility. It produces symptoms similar to those of metallic mercury.

When calomel is acted upon by ammonium hydroxid, a black compound is formed having the formula NH_2Hg_2Cl, which is called dimercurous ammonium chlorid. This action is characteristic, and serves to distinguish this chlorid from the other insoluble chlorids.

Mercuric chlorid or corrosive sublimate received its name because of its corrosive action on animal tissues and the fact that it was originally prepared by the process of sublimation. (Any substance is a sublimate if it is produced from a solid or solids by converting it, or some product of the action, into a vapor, and condensing the resulting substance on the cooler parts of the vessel used. The process is called sublimation.) The compound is manufactured by subliming mercury sulfate ($HgSO_4$), with common salt ($NaCl$). (Write reaction.)

Mercuric chlorid is soluble in water, ether, and alcohol. Ether will readily remove it from its water solution. Ammonium hydroxid forms with it in its water solution a compound in which one atom of chlorin of the chlorid is replaced by NH_2; or it may also be regarded as ammonium chlorid (NH_4Cl), in which two atoms of hydrogen are replaced by one atom of mercury. This compound is white, and this fact

makes mercuric chlorid readily distinguishable from the mercurous chlorid.

Like all elements possessing a variable valence, mercury is capable of being oxidized and reduced when in combination. Its most stable salts (in the air) are the mercuric compounds. Oxidizing agents readily change the mercurous compounds to the mercuric form. This has been illustrated in studying the action of dilute and concentrated nitric acid on mercury with or without the aid of heat. The action of an excess of the halogens on the (-ous) compounds is another illustration. On the other hand, reducing agents convert the mercuric compounds to the mercurous compounds or to metallic mercury. This is shown by the action of stannous chlorid ($SnCl_2$), on mercury chlorid. The stannous chlorid becomes stannic chlorid ($SnCl_4$), a gain of two units of valence for the tin, while each atom of mercury loses one or two, according to whether the mercury is in the form of mercurous chlorid or free mercury.

Mercuric chlorid is a powerful antiseptic and disinfectant, and is much used in surgery to disinfect the vessels used and the hands of the operator before performing surgical operations.

Mercuric chlorid is a very active poison, well deserving the name corrosive sublimate: 30 mg. of the chlorid are sufficient to produce marked poisoning effects, and often is sufficient to produce death. The best antidote[1] for the poisoning pro-

[1] The general idea of an antidote is that it is a substance that counteracts the action of a poison, either by rendering it inert or by setting up in the system some action that in some way (often little understood — the so-called physiological antidotes) counteracts the effect of the poison. In a large number of cases the antidote is effective because it forms with the poisonous substance an insoluble compound, as in the case just mentioned. Sometimes the antidote prevents the poisonous substance from coming in contact with the walls of the stomach. This is often the case when oily substances are used as antidotes. In case the poisoning is by acids, some carbonate or oxid may be used. Care must be used in selecting the carbonate to be used, since the heat of reaction may be sufficient to produce serious results. For alkalis only the weakest acids and in dilute form can be used, such as vinegar. Fats and oils are also useful here.

duced by this and other soluble salts of mercury is the albumen (or white) of an egg. The white of the egg should be beaten up with water or milk, and swallowed as soon as possible after the poison is taken into the stomach. The albumen forms an insoluble substance with the mercury compound, and can thus be removed from the stomach by an emetic or by the use of the stomach pump.

The other halogen salts, *i.e.* the iodids and bromids, are insoluble in water, and are formed by the direct union of the elements or by treating soluble salts of mercury with a soluble iodid or bromid, usually potassium or sodium iodid or bromid. Mercuric iodid, for example, is soluble in an excess of the reagents, forming the double salts, $2\,KI.HgI_2$, or $KI.HgI_2$, according to conditions.

An interesting fact in connection with the solutions of these double iodids is that they are colorless, or nearly so, while the solid iodid is a red compound. When this solution is made alkaline by a fixed alkali, it forms a very delicate reagent for free ammonia. This is Nessler's reagent.

The reaction is —

$$4\,NH_4OH + 2(2\,KI.HgI_2) = NH_2Hg_2IO + 3\,NH_4I + 3\,H_2O + 4\,KI.$$

The insoluble compound is called dimercur-oxy-ammonium iodid, and is brown in color.

Mercury Sulfids. — Mercury forms the two sulfids that are indicated by its valence; namely, Hg_2S and HgS. It is, however, questioned at present whether the precipitate formed by hydrogen sulfid acting on soluble mercurous salts is not a mixture of mercuric sulfid (HgS) and free mercury; *i.e.* some of the mercury is oxidized, and some of it has been reduced. This sulfid (Hg_2S) is formed when sulfur is ground up with mercury, but is soon separated, on standing, into mercury and mercuric sulfid (HgS).

Mercuric sulfid has been mentioned as the principal ore of

mercury. It is known as cinnabar, and occurs in both red and brown colored masses. The brown cinnabar becomes red if it is powdered and heated for some time to a temperature of about 50° in a solution of sulfur in potassium hydroxid. The sulfid is prepared by the action of hydrogen sulfid on a soluble mercuric salt. The precipitate frequently undergoes several characteristic changes in color while it is forming, but when an excess of the reagent is present, it becomes black. These different colored compounds are due to the combination of the normal sulfid that is formed at first with the salt of mercury that has not been changed. For example, if the salt in solution is mercuric chlorid, a compound of the formula $2\,HgS.HgCl_2$ is formed. This compound soon decomposes if more of the sulfid is used. This black sulfid is changed to a red color if it is dried and sublimed out of contact with the air. The red sulfid of mercury is used as a pigment in painting. Its value as a pigment depends on its brilliancy of color and its power to resist the action of the usual atmospheric agents, retaining its color in presence of hydrogen sulfid, oxygen, carbon dioxid, sulfur dioxid, etc., while minium, tri-plumbic tetroxid, and other red pigments are blackened or bleached.

Mercuric sulfid is insoluble in nitric acid, while all the other sulfids (except those of arsenic, tin, antimony, gold, and platinum) are dissolved. The sulfids of antimony and tin are decomposed by nitric acid, but insoluble oxids are formed.

This fact is made use of in separating mercury from the sulfids of the elements of the second groups of elements. (See later on.)

Mercuric sulfid readily dissolves in aqua regia, and when the excess of the acid is driven off and the residue dissolved, the usual test for mercury can be made. (See last study, No. 6.)

Mercury Nitrates. — Both mercurous and mercuric nitrates are readily formed by the action of nitric acid on the metal. If the acid is dilute, and is used at ordinary temperature, the

product is mostly the mercurous nitrate ($HgNO_3$). Concentrated nitric acid forms mostly mercuric nitrate under the same conditions. The oxidation is complete if heat is used.

Both these salts are decomposed by water, forming basic nitrates,[1] the composition of which varies, depending on the conditions under which they are formed. One of the salts formed by mercurous nitrate has the composition represented

[1] The term *basic salt* or *compound* has been used several times, and the student is now in condition to understand its application. A salt has been defined as a compound produced by the action of an acid on a base, an oxid, or a metal. (See pages 100 and 357, Part I.) Or a salt is a compound formed by replacing the hydrogen of an acid by a metal. In monobasic acids only one such compound can be formed, while in dibasic, etc., acids a portion only of the hydrogen may be replaced by a metal, thus forming two or more salts. Acids have been regarded as made up of two groups; namely, the hydroxyl group and the negative acid group or residue. For example, nitric acid is $HO-NO_2$. The negative acid residue, NO_2, is combined with the hydroxyl, which is usually negative, and is always so towards metals. Therefore, when a base reacts with an acid, the more positive metal replaces the hydrogen of the acid hydroxyl. We may regard these changes from another standpoint; namely, that the hydrogen of the base (hydroxid) is replaced by the negative acid residue, and that only a part of such hydrogen is thus exchanged. For example, lead hydroxid has the formula $Pb{<}^{OH}_{OH}$. If the hydrogen of one of these hydroxyl groups is replaced by NO_2, the compound $Pb{<}^{OH}_{O-NO_2}$ is formed. Such salts are called basic. They always have more of the metal than the corresponding normal salt contains. In some cases these basic salts contain no hydrogen, as in case of the basic lead acetates (which see). Examples of these basic salts will be given as the study of metals progresses. (Compare with acid salts.)

There is a class of hydroxids that are basic in the sense that they contain more of the metal than does the normal hydroxid. For example, lead hydroxid, formed in the usual way, is basic, *i.e.* it is $Pb_2O(OH)_2$, or it may be represented thus: —

$$\begin{array}{l} Pb-OH \\ \quad\diagdown \\ \quad\quad O \\ \quad\diagup \\ Pb-OH \end{array}$$

Another recognized hydroxid is represented by this formula: —

$$\begin{array}{l} O\diagup Pb-OH \\ \quad\diagdown \\ O\diagup Pb \\ \quad\diagdown Pb-OH \end{array}$$

by the formula $HgNO_3.HgOH$. The presence of a little nitric acid and mercury prevents the formation of this compound. Mercuric nitrate forms the basic salt represented by the formula $Hg(NO_3)_2.2\,HgO.2H_2O$. Free nitric acid prevents the formation of this compound. Mercurous nitrate is readily oxidized to the mercuric form.

Mercury Sulfates. — The two sulfates of mercury are made by the action of sulfuric acid on mercury or on the oxids of mercury. When the mercury is in excess and gentle heat is used, the product is mostly mercurous sulfate (Hg_2SO_4). When an excess of concentrated sulfuric acid and high heat is used, the product is mercuric sulfate ($HgSO_4$). Both salts are decomposed by much water with the formation of basic sulfates, $Hg_3O_2SO_4$ (or $2\,HgO.HgSO_4$), and sulfuric acid.

These hydroxids form salts by the replacement of the hydrogen of the hydroxyl by an acid residue. One of the lead acetates mentioned on page 46 is formed by substituting the acetic acid residue or radical C_2H_3O (acetic acid is $HO-C_2H_3O$) for both atoms of hydrogen of the hydroxyl of the basic hydroxid, $Pb_3O_2(OH)_2$. Whether these basic salts are regarded as formed by the combination of an acid with a larger proportion of a base than is the case in a normal salt, or as a metallic hydroxid in which the hydrogen of the hydroxyl is replaced by an acid residue, there is no law which governs their formation such that the composition of the salt can be correctly known from the usual facts. For example, the formula for lead sulfate is $PbSO_4$, and for any normal bivalent element it is MSO_4, while there are several basic lead carbonates and acetates, the composition depending within certain limits on the conditions under which they are produced. The formula for each compound must be determined by itself.

Double salts are normal salts of poly-hydrogen acids in which the hydrogen is replaced by more than one metal, usually by only two; or they are salts in which the hydroxyl of metallic hydroxids is replaced by different acid residues. For example, such a salt is $(PbCl)_2CO_3$, or

$$\begin{matrix} Pb-Cl \\ \diagdown \\ \quad CO_3 \\ \diagup \\ Pb-Cl \end{matrix}$$

The latter class of salts are less common than are those of the first class. Microcosmic salt illustrates the first class. It has the formula NH_4NaHPO_4, or it is ammonium sodium hydrogen phosphate.

The other salts of mercury are of little interest. They are mostly insoluble compounds readily decomposed by water, forming basic salts. These are the phosphates and carbonates. The borate and silicate have not yet been formed.

Experimental Study, No. 7. — (*a*) To 20 cc. of a mixture of the soluble salts of silver, lead, and mercury (-ous) (nitrate or acetate) add hydrochloric acid as long as any precipitate is produced. Of what will it consist? Filter out the precipitate, and wash once with cold water. Save the filtrate and call it

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Still another class of salts is formed, in which there is an excess of the acid residue in the compound. They differ from acid salts in that all of the hydrogen of the acid has been replaced. They are called pyro-salts, from the fact that they are made by heating the salts (or their acids) until either water or what corresponds to it is driven off. For example, magnesium ammonium phosphate ($MgNH_4PO_4$) when heated gives off ammonia and water and leaves $Mg_2P_2O_7$. (See PYRO-ACIDS, Part I.)

The basic salts are formed by the action of water on the normal salts or by the action of these salts on the oxid or hydroxid of the metal. Basic lead acetate is made by boiling lead oxid in a solution of lead acetate. Water often decomposes normal salts; usually one-half of the hydrogen of the former unites with the acid or salt group to form the acid of the salt, and the hydroxyl enters the salt molecule to form the basic salt. Take, for example, the action of water on mercurous nitrate, which is represented by the following reaction: —

$$2\,HgNO_3 + H_2O = HgNO_3.HgOH + HNO_3.$$

Here it is seen that one molecule of nitric acid is formed for each two molecules of the nitrate that is decomposed. If one of these normal salts is put into water that already contains a certain amount of the free acid corresponding to that of the salt, then no basic salt is formed. On the other hand, if the acid formed by the decomposition is washed away by pouring water over the insoluble basic salt, the change may be completed, and the hydroxid of the metal is left.

It will be noticed as the study progresses that the basic salts are formed with metals that have weak basic properties. Strong bases like sodium and potassium never form basic salts, but, on the other hand, they readily form acid salts. Weak acids also readily form the pyro-salts, especially with the stronger bases. The weak bases do not form stable salts with weak acids at all, or if they are formed, they are easily decomposed and are always basic. The basic salts break up at comparatively low temperature, water being the first to leave the molecule if they were formed by the action of water on a normal salt.

No. 1. Next add 50 cc. of boiling hot water to the precipitate on the filter paper. After the water has run through the filter, boil it again and allow it to pass through the filter. What has been removed by this hot water? Save the filtrate and mark it No. 2. Pour on the residue as much more boiling hot water. Reject this filtrate. What is left on the filter paper? (See previous studies.)

Next gently warm 10 cc. of ammonium hydroxid, and pour it on the residue. Repeat the operation, using the same solution. What is the action of the ammonium hydroxid? Call this filtrate No. 3. To a portion of filtrate No. 3 add nitric acid until the solution is acid. Explain result. Nearly neutralize another portion, and add a few drops of K_2CrO_4. Explain.

Add to a portion of filtrate No. 1 a few drops of K_2CrO_4 solution. Explain. Examine filtrate No. 1 with solutions of $K_2Cr_2O_7$ — K_2SO_4 and KI. Explain the results. What is the black residue left on the first filter paper? Explain and write all the reactions produced in this study.

(*b*) Suppose H_2SO_4 or a solution of K_2SO_4 had been used with the original mixture, what would have been the result? Explain. If the precipitate produced is filtered out, and a solution of NaCl added to the filtrate, what does the result mean? Explain how the metals are now distributed. How could you prove the presence of each of the metals?

(*c*) Add to the original mixture nitric acid, and boil until the precipitate produced by adding a solution of NaCl to 2 or 3 cc. is not blackened when ammonium hydroxid is added. What change has been produced? What element has been removed? Write the reaction for the mercury salt. Next add a solution of NaCl to the whole solution as long as a precipitate is formed. What is the precipitate? Filter, and treat the precipitate as in (*a*). To a portion of the filtrate add KOH until the solution is alkaline. What is the precipitate? To

another portion add a solution of KI, after nearly neutralizing the excess of acid. Explain.

(*d*) Suppose you had added ammonium hydroxid in excess to the original solution (nitrates), what would have occurred? Filter and wash the precipitate into a beaker, and treat with dilute sulfuric acid, and heat. Explain the result, and recognize each metal.

ARSENIC.[1]

Experimental Study, No. 8. — (*a*) Pass hydrogen sulfid into a solution of sodium or ammonium arsenite for several minutes. Next add sufficient hydrochloric acid to acidify the solution, and if necessary to complete precipitation, pass in more gas. The precipitate is As_2S_3. Explain how the acid aids in producing the precipitate. From what elements is the arsenic removed? With what element will the sodium unite? Filter out the precipitate, and evaporate a portion of the filtrate to dryness in order to be sure that all the free acid has been drawn off. Dissolve the residue, and test it for hydrogen chlorid. How was the chlorin combined? Wash the precipitated sulfid to remove the acid, transfer a portion to a test-tube, and add yellow ammonium sulfid.[2] Warm. The compound formed is $(NH_4)_3AsS_3$. Write the reaction. Compare this formula with that of ammonium arsenite. How does it differ? Treat this solution with a few drops of dilute sulfuric acid. Treat a dilute solution of the ammonium sulfid with the dilute acid. Compare the result. What is the precipitate in each case? Note the difference in the filtering of the two precipitates. Add an

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[1] For the study of arsenic and its compounds, see Part I., pages 159 and 273.

[2] Yellow ammonium sulfid will always be meant when this sulfid is mentioned, unless otherwise stated. It is made by adding sulfur to ammonium hydroxid, and passing hydrogen sulfid through the solution until it is saturated.

excess of a solution of ammonium carbonate to another portion of the arsenious sulfid. Warm slightly. The reaction is —

$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3\,H_2O.$$

Slightly acidify the solution. What is the precipitate?

(*b*) Acidify with HCl a solution of an arsenate, and pass in hydrogen sulfid for at least an hour. Note the difference in the manner of this precipitation and that in (*a*). Arsenious sulfid, As_2S_3, and free sulfur are formed. Why the free sulfur? Write the reaction. What element is reduced? What one oxidized?

(*c*) To a solution of an arsenite add silver nitrate solution. Note the color of the precipitate. Write the reaction.

(*d*) Treat a solution of an arsenate in the same manner, and note the precipitate, etc.

(*e*) To a solution of an arsenite (or to arsenious oxid suspended in water) add nitric acid, and boil for several minutes. Neutralize, or evaporate off, the excess of acid, and test the solution as in (*c*). Write the reactions. What is the source of the oxygen? What was the evidence of change? Was it due to the treatment with nitric acid?

(*f*) To a solution of an arsenite add a solution of sodium hydrogen carbonate, and follow it by a solution of iodin in potassium iodid; stir well, and add the iodin solution until only a slight color remains. Boil for a short time. Add ammonium hydroxid and a solution of magnesium sulfate. Treat a solution of an arsenite and a solution of an arsenate with the latter reagents, and compare the three. The result serves to distinguish an arsenite from an arsenate. The compound formed is $MgHN_4AsO_4$. Compare also the silver salts of these acids. What was the action of iodin here? Treat a portion of the solution with chlorin water. Explain the result. How was the iodin combined in the new compound? What is the use of the sodium carbonate?

(*g*) To a solution of an arsenate add one of sulfur dioxid, or

pass the dioxid into the solution until it is saturated. Boil this solution until all the excess of the gas has been driven off. To a portion of the solution add a little ammonium hydroxid and then silver nitrate. Compare with (*c*). Test the other portions of the solution for sulfuric acid. The two results mean what? What is the residue? What is oxidized?

Acidify another portion of the solution and pass in H_2S.

(*h*) To a solution of an arsenite add copper sulfate solution. (Same treatment for an arsenate.) $CuHAsO_3$ and $CuHAsO_4$ are formed. Write reactions.

(*i*) To a boiling solution of copper (-ic) acetate, add a solution of an arsenite. Boil for some time. The precipitate is "Paris green."

$$3\,Cu(AsO_2)_2.Cu(C_2H_3O_2)_2.$$

(*j*) To a solution of an arsenite add a solution of $FeCl_3$. (Same treatment for an arsenate.)

(*k*) Dissolve a little As_2O_3 in HCl, and place in the solution pieces of bright copper. After leaving the copper in the solution for some time, carefully remove and dry them. Transfer the copper strips to a dry test-tube, and heat to low red heat. What is the deposit on the cool parts of the tube? Was the copper changed? Examine the solution, or retain it for such study until the study of copper is taken up. Examine the deposit on the glass with a magnifying instrument. Remove the deposit, dissolve it in a little nitric acid, and add slight excess of ammonia. Drive off the excess of alkali, and add a solution of silver nitrate. The result shows what? Write equations for all these reactions.

(*l*) Repeat (*a*) and (*i*) of Experimental Study No. 32, Part I.

General Statement as to Arsenic and its Compounds. — The facts learned in the preceding study are mainly those that are used in qualitative analysis.

The poisonous properties of arsenic and its compounds, and their frequent use in medicine and for criminal poisoning, make it necessary that there shall be accurate and delicate methods for its determination and recognition. If the arsenic compound is unmixed with organic substances, it can be detected by the methods just studied, especially by (*a*), (*b*), (*c*), (*d*), and (*l*). If the arsenic compounds are mixed with organic matter, — for example, the contents of a stomach, — it must be separated from such substances before the usual tests for its recognition can be made. It is usual to add to the organic material, whether liquid or solid, about 20 cc. of concentrated hydrochloric acid, and digest at a temperature of 60° for an hour or more. The liquid portion of the resulting action is separated by decantation or by filtering it through fine, clean cotton or linen cloth. It may be refiltered through ordinary filters. Strips of bright copper are placed in this solution and heated for some time. The copper is now removed and very carefully washed, dried, and placed in a test-tube, and proceeded with as in (*k*) of this study. (See also under ANTIMONY.)

Or, again, the organic matter may be destroyed by chlorin produced by the action of hydrochloric acid on potassium chlorate. This leaves the arsenic in the form of an arsenate. This arsenate may be recognized as such, or it may be reduced by sulfur dioxid and precipitated by hydrogen sulfid, and further examined by (*l*).

The acids of arsenic form salts with all the stronger bases, most of which are not, however, of general interest. Some of the salts of copper are beautiful green pigments, and are used for this purpose in paints, for coloring wall paper, and in many other ways. The principal greens are known as "Paris green" and Scheele's green. The former compound is copper arsenite and acetate, $3\,Cu(AsO_2)_2.Cu(C_2H_3O_2)_2$, and the latter is copper hydrogen arsenite ($CuHAsO_3$). It was first produced by the Swedish chemist Scheele; hence its name. Paris green

is used quite commonly as an insecticide. A solution of potassium arsenite is used in medicine, and is known as Fowler's solution.

Magnesium ammonium arsenate ($MgNH_4AsO_4$), silver arsenate, and arsenite are of interest because of their connection with analytical chemistry.

ANTIMONY.[1]

General Statement. — Antimony stands in an intermediate position in reference to the metals and non-metals. It forms salts with the halogen acids and with some of the ternary acids. It also forms salts with many organic acids. The inorganic salts are, in general, quite unstable. The fixed alkali antimonates are, however, quite stable and are quite insoluble. Its basic character is far more marked than is that of arsenic. Its halogen salts are partially decomposed by water, forming oxychlorids, or basic salts; *i.e.* oxygen replaces two atoms of chlorin ($SbOCl$), while arsenious chlorid is wholly decomposed, as has been previously shown. It resembles tin and bismuth in its capacity to act both as a base and an acid, the lower oxid being generally basic and the higher oxid being always acidic. It also, like arsenic and tin, forms sulpho-salts, corresponding to the oxygen salts, the sulphur taking the place of the oxygen. For example, K_3AsO_4 and K_3AsS_4, K_3SbO_4 and K_2SbS_4.

Its valence is like that of arsenic and bismuth; *i.e.* it is 3 and 5. The lower form can be changed to the higher, or the higher to the lower form, by means of oxidizing and reducing agents.

Experimental Study, No. 9. — (*a*) Heat a small amount of powdered antimony in the air on charcoal for a short time. What is the white residue?

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[1] For a study of the element and its binary compounds, see pages 167–173, Part I.

(*b*) Heat some powdered antimony with nitric acid, or fuse it with potassium nitrate in a small porcelain crucible. Note and explain all the changes that occur. Wash and filter out the white residue produced in the first action. Heat a little of this powder on charcoal, covering the powder with sodium carbonate. What is the globule? Explain the action of the charcoal and of the carbonate. (If the antimony is fused with the potassium nitrate, remove the mass from the crucible, powder it, and boil with water. The insoluble residue is filtered out, and it can be examined as was directed for the oxid produced in the first case.)

(*c*) Dissolve some of the oxid in hydrochloric acid, and evaporate to expel the excess of acid. What is the residue? Add an excess of water to a portion of this residue, and note any changes that may occur. Filter out the precipitate, and test solution for hydrogen chlorid. Pass H_2S through a portion of this solution. (See (*d*).) Is the acid free or combined? Test with litmus paper. Transfer some of the precipitate to a test-tube, and treat with hydrochloric acid. Next add cold water to the solution. Treat a portion of the original residue with a fairly dilute solution of hydrochloric acid; also another portion with a concentrated solution. Treat 10 cc. of each of the solutions with water, and note the quantity of water used before any precipitates are formed. The precipitate is SbOCl, antimony oxy-chlorid or antimonyl chlorid, if cold water is used, and $Sb_4O_5Cl_2$, if hot water is used. Write the reactions, accounting for the oxygen in the new molecule. Where is the chlorin? (See under BASIC SALTS.)

(*d*) To some freshly precipitated antimonyl chlorid (filtered and washed) add a solution of sodium carbonate as long as any effervescence occurs. What is the gas that escapes? Prove it. Filter out and wash the precipitate and test the solution for hydrogen chlorid and antimony. (See (*d*).) Is the acid free? With what is it combined? What was the cause of the effer-

vescence? Treat a portion of the precipitate with silver nitrate solution. Is there any evidence of change? Wash the precipitate free of the nitrate, and expose it to the light; is there any evidence of the formation of silver chlorid? Treat the oxychlorid in the same way. If the precipitate is antimony trioxid (Sb_2O_3), what is the reaction? Write reactions. Save the compound just formed for later study.

(*d*) Pass H_2S into a solution of "tartar emetic," potassium antimonyl tartrate ($KSbOC_4H_4O_6$). When the solution is saturated with H_2S, add a few drops of hydrochloric acid. Compare the result with (*a*) Study No. 8. Explain this action. Write the reaction. Filter and wash the precipitate, and examine portions of it as the arsenious sulfid was examined in (*a*) of Study No. 8. Treat a portion of the sulfid with concentrated hydrochloric acid, and boil. What gas escapes? Write the reaction. How does the acid act on arsenious sulfid? Carefully note all the results in the work just indicated.

(*e*) Repeat Study No. 34, Part I. How could arsenic be separated from antimony when their soluble compounds are mixed, using the facts just determined? Use also (*k*) of the last study modified as follows: When the copper has been sufficiently long in the solution of the antimony compound, remove and wash it free from the substances of the solution, and boil it in a dilute solution of NaOH, to which has been added a few drops of a solution of potassium permanganate. Turn off the solution, slightly acidify with HCl, and pass in H_2S. Explain the use of each reagent. The permanganate furnishes oxygen. For what?

(*f*) To an acid solution (HCl) of an antimony compound add a piece of metallic zinc, allow the action to proceed for a few minutes, observing whether there is any deposit on the zinc. Next add a piece of platinum foil, bringing it in contact with the zinc. Note any differences in the action. Remove the foil after a few minutes and treat it with HCl. Warm. Note

any changes. Remove and carefully wash away the acid and treat with nitric acid. The compound $HSbO_3$ is formed.

(*g*) Treat the trioxid formed in (*c*) with nitric acid and evaporate to dryness, in an evaporating-dish. Note the changes in this oxid. It has become antimony pentoxid (Sb_2O_5). Boil some of the yellow powder in water for some time. Test the solution with litmus. Treat another portion of the powder with potassium hydroxid, and heat. The compound formed is potassium antimoniate ($KSbO_3$). Boil another portion of the pentoxid with concentrated hydrochloric acid. When it has been dissolved, add much water to the solution. The white precipitate is pyro-antimonic acid ($H_4Sb_2O_7$).

(*h*) Use KOH, NH_4OH, K_2CO_3, and $(NH_4)_2CO_3$, on a solution of an antimony salt. $Sb(OH)_3$ is formed in each case. The precipitate is soluble in excess of the carbonate, and of potassium hydroxid. What is formed? Write the reactions.

(*i*) To a solution of "tartar emetic" add a solution made from tea. Add to a like solution tannic acid or a solution from nutgalls. Note the results.

Compounds of Antimony.

(*a*) **Oxids and Hydroxids.** — It has been previously shown that the valence of antimony for hydrogen is 3, and for chlorin it is 3 and 5. Therefore antimony would be expected to form two oxids represented by the formulæ Sb_2O_3 and Sb_2O_5 respectively. Two oxids are known, the results of the quantitative analysis of which agree with the formulæ just given; *i.e.* the proportions of antimony and oxygen formed by this analysis agree with the atomic mass proportions of 240 parts of antimony to 48 or to 80 parts of oxygen. Another oxid is formed when the trioxid or pentoxid is heated to fusion in the air. Analysis shows that it has the formula Sb_2O_4 or $SbO_2 - SbO_2$. These oxids are but slightly soluble in water, the tetroxid being

the most soluble. The latter oxid when heated in water dissolves sufficiently to give an acid reaction with litmus.

The trioxid and pentoxid are both soluble in alkaline hydroxids, forming salt-like compounds having the formulæ $KSbO_2$ and $KSbO_3$. The first-named oxid is only slightly acidic, and its most stable compounds are basic. The pentoxid is always acidic in character, and forms acids corresponding in form to that of the corresponding oxid of phosphorus. They are H_3SbO_4, $HSbO_3$, $H_4Sb_2O_7$. These are named antimonic, metantimonic, and pyro-antimonic acids. The first acid is unstable, and it is claimed by some writers that it does not exist. It is formed by the action of hot water on the pentachlorid of antimony, and by dissolving antimony in aqua regia. The salts of the latter two acids are stable. The disodium pyro-antimonate is very insoluble, and is the most insoluble salt of sodium.

(*b*) **Salts.**—The salts of antimony are formed from the normal hydroxid ($Sb(OH)_3$) or from the oxy-hydroxid (SbO.OH). When these hydroxids are treated with the stronger acids, they form salts in the usual manner; *i.e.* the hydrogen of the hydroxyl is replaced by the acid radical. The salts formed with the latter hydroxid therefore takes the form (SbO)X. For example, tartar emetic has the formula $(SbO)KC_4H_4O_6$. They are distinguished as antimonyl salts.

Sulfids of Antimony.—Antimony forms two sulfids, corresponding to the two oxids. The trisulfid (Sb_2S_3) is found in nature and is known as stibnite. It is produced by the action of hydrogen sulfid on an acid solution of compounds containing trivalent antimony. The natural sulfid is a grayish crystalline substance. The orange-red sulfid produced by precipitation is changed to a nearly black crystalline substance by heating to 200°.

The pentasulfid is produced by the action of hydrogen sulfid on antimony pentachlorid or by the action of an acid on a sulfo-

salt of antimony, in which the antimony is quinquivalent. For example, —

$$2(Na)_3SbS_4 + 6\,HCl = 6\,NaCl + Sb_2S_5 + 3\,H_2S.$$

This sulfid, like the corresponding one of arsenic, is decomposed into the trisulfid and sulfur dioxid when heated in the air to temperatures below red heat. Both of these sulfids dissolve in the three soluble alkaline sulfids to form the corresponding sulfo-salts already mentioned.

There is an oxy-sulfid of antimony (Sb_2OS_2) that is used in dyeing, under the name of antimony vermilion, because of its brilliant red color.

The native trisulfid is not only a source of the antimony of commerce, but it is used in matches, in friction tubes, and in colored fires, in connection with potassium chlorate. The pentasulfid is used in medicine, and is known as sulfur aurantum.

The compounds of antimony are poisonous and have often produced death. Antimony trichlorid, butter of antimony, is caustic in its action and is sometimes used in surgery for that purpose. The soluble compounds are all very irritating to the mucous membrane of the alimentary canal, and this is especially true of tartar emetic ($SbOKC_4H_4O_6$), which produces violent vomiting when swallowed. The element can be detected by methods given in Study No. 9.

The method of testing for arsenic by means of copper can be applied to antimony compounds. The bright copper becomes coated with the metallic antimony. When this is dried and heated, it does not volatilize or produce volatile product. If the coated copper is boiled in a solution of sodium hydroxid, to which has been added some oxidizing agent like potassium permanganate, the antimony is oxidized and converted into potassium antimonite ($KSbO_2$) which is in solution. The clear solution is slightly acidulated with hydrogen chlorid, and hydrogen sulfid is then passed into the solution. The production of

antimony sulfid is evidence of the presence of antimony. The potassium antimonite can be acidified and transferred to the hydrogen generator, and the antimony recognized by methods given in Part I., page 170. See the same reference for the separation and recognition of antimony and arsenic.

The antidote for antimony poisoning is a solution containing tannin, such as solutions of tea, coffee, nutgalls, oak bark. Emetics should be given before and after the use of the mentioned solutions. The use of these antidotes is illustrated by (*i*) Study No. 9.

TIN (STANNUM).

Occurrence and Distribution. — Tin has not been found free in nature, but occurs combined with oxygen in a mineral known as cassiterite, or tin stone, or stannic oxid (SnO_2). It is not widely distributed, but is found in England, Germany, Malay Islands, India, Australia, and in the United States in Dakota and California. It is found in veins or lodes and in the beds of streams of water, and is then known as "stream tin." The cassiterite has been transported by the water which has flowed over the veins containing it.

Preparation. — Tin is easily prepared from its ore by the removal of its oxygen by means of carbon. The ore contains many impurities, but these are much lighter than the oxid and are mostly separated by mechanical means. The ore is crushed into a fine powder and washed down planes so inclined that the lighter impurities are carried away. The pure cassiterite has a specific gravity of 6.9, while the impurities are nearly all much lighter (2.5 to 3). The tin stone thus obtained may yet contain sulfur compounds of arsenic, iron, antimony, copper, etc. It is next roasted, by which the sulfur and arsenic are driven off. (In what form?) The resulting mass is now mixed with

coal (anthracite) and some lime, and heated in proper furnaces until the tin is set free. It is removed from the furnace in the liquid form. The lime (CaO) forms a fusible substance (slag) with most of the impurities remaining. Tin produced in this manner often contains small quantities of other metals alloyed with it. It is further purified from these metals by slowly melting the first product and allowing the more fusible tin to flow away, leaving the less fusible mass behind. The absolutely pure tin is produced by reducing the pure oxid.

Experimental Study, No. 10.—(*a*) Grind thoroughly together some oxid of tin with about its own volume of charcoal, place it in a clay crucible, and cover it with sodium carbonate. Heat the crucible to a bright red heat, continuing the heat for some time after the whole mass is fused. When it has cooled, break the crucible and examine the contents. Explain the use of each substance.

(*b*) Spread a piece of pure tin foil on a plate of glass that has been made chemically clean by acids and alkalis and thoroughly washed with water. Now bring a small globule of mercury into the centre of the foil. Note the action of the mercury. Cover with a plain piece of board, and place weights on top of this and leave for a few hours. Examine the result. Why must the glass be clean? Of what use is the mercury? Why are weights placed on the glass?

(*c*) Melt a small piece of tin and add about the same amount of lead. Cool and examine the mass. Did the tin oxidize before fusing? Why not melt lead and add the tin to it?

(*d*) Clean a piece of copper and melt a piece of tin on the copper, or plunge clean copper wire into molten tin. (Same for iron wire.) Place a few drops of hydrochloric acid on the surface of the copper and rub molten tin over the surface. What was the use of the acid? Is this an alloy? Try to scrape off the tin.

(*e*) Treat pieces of granulated tin with concentrated HCl. Same treatment with sulfuric and nitric acids. Use both dilute and concentrated nitric acids. What gas escapes? How do these actions compare with the actions of these acids on the other metals studied? With nitric acid stannic oxid (SnO_2), is produced. Write the reactions.

(*f*) Mix thoroughly powdered tin and sulfur (1 part of sulfur to 3.7 parts of tin) and heat in an ignition tube. Examine the resulting substance. What is it? Heat some of the substance with hydrochloric acid and note the escaping gas. Write the reactions.

(*g*) Heat a little stannic chlorid in a test-tube and note the changes.

(*h*) Place a piece of zinc in a solution of stannic chlorid in cold water. Leave for several hours. Write the reactions.

(*i*) Heat a piece of bright "tin" (used for "tinware") to about the fusion point of the tin coating, and suddenly cool by plunging into cold water. Next pour over the surface aqua regia, leave for a short time, wash off the acids, and treat with a solution of sodium hydroxid and rinse again. Explain.

(*j*) Evaporate to dryness a portion of the solution of tin in hydrochloric acid. Be sure and drive off all the free HCl. Prove the presence of combined acid. To a portion of the solution add a solution of bismuth chlorid. Next add a fixed alkali hydroxid until the solution is alkaline. Note the result. This is a delicate test for either bismuth or for stannous chlorid.

Pass chlorin gas (or add chlorin water) through another portion of the acid solution until the solution becomes saturated. Heat until all the free chlorin is driven off, adding water and acid if necessary to keep the substance in solution. When the free chlorin is driven off, add to a portion of it bismuth chlorid solution and alkali to alkalinity. Note and compare the result with first case. What is the possible cause of this difference? Hydrogen sulfid may be passed into slightly acid

solutions in each case. Also treat a portion of each solution with mercuric chlorid solution. The results show what in reference to their compounds? (See under ATOMIC MASS AND VALENCE.)

(*k*) Add a solution of iodin to a solution of stannous chlorid. Add it slowly and note changes in the color of the solution. A few drops of starch solution may be added to the stannous chlorid solution. How will the free iodin act on the starch? What has become of the free iodin? Pass H_2S into the solution until all the tin is precipitated. Filter, and add chlorin water to the filtrate. Explain and write all the reactions.

Physical Properties. — The element tin is a silver-white substance harder than lead, yet soft enough to be easily hammered and rolled. It can be rolled into very thin sheets which are known as tin-foil, although most of the tin-foil of commerce is an alloy of tin and lead. Its specific gravity is a little less than that of iron, and is 7.29. It is crystalline in structure, which is modified when it is cooled to temperatures below the freezing-point of mercury. Under these conditions it appears to separate into distinct crystals, and is broken up into a powder when struck a slight blow. If it is remelted and cooled, it returns to its usual condition. It is also brittle near its melting-point. The fact of its crystalline structure is shown when a bar of it is bent back and forth. The rubbing of the surfaces of the crystals over each other produces a peculiar sound call the "tin cry." It melts at 228°, and is vaporized at about 1500°.

Tin alloys readily with nearly all of the metals and forms many very useful substances.

Chemical Properties. — Tin is not chemically active towards most other elements at ordinary temperatures. It is not attacked by the oxygen of the air until it is heated to near its fusing-point, when it slowly oxidizes. At higher temperatures, it unites with oxygen with great rapidity. It is not attacked

by the acids of fruits, vinegar, etc., thus making it useful for dishes employed for cooking-purposes, etc. At red heat, it decomposes water, forming tin oxid and hydrogen.

The element readily dissolves in hydrochloric acid, forming tin chlorid and hydrogen. Concentrated sulfuric acid acts upon this metal only at high temperatures, producing the usual products of the action of this acid on metal. Often, however, the reduction of the sulfur is completed and hydrogen sulfid is formed. Nitric acid oxidizes the metal, but does not form the nitrate under these conditions. The fixed alkalis attack it in hot concentrated solutions, forming alkali salts. (See later on.)

The halogens and sulfur unite directly with tin at high temperatures, forming the corresponding binary compounds.

Name and History. — Tin has been known from the early times, probably because of the ease with which it can be prepared from its ore. It was not at first wholly distinguished from lead, and was called shining white plumbum to distinguish it from black plumbum. The word *stannous*, from which the symbol Sn is derived, was used as early as the first part of the present era. The name *cassiteron* connects it with its ore cassiterite. The ancient peoples used it alloyed with copper in a substance now known as bronze. The metal was used in large quantities by the Phœnicians and Romans.

Atomic Mass and Valence. — Tin forms several volatile compounds from which the atomic mass can be easily calculated. Among these compounds are two chlorid compounds and an organic compound, stannic ethid ($Sn(C_2H_5)_4$). The higher chlorid has a vapor density of 129.64. The compound contains 45.44 per cent of tin and 54.56 per cent of chlorin. The lower tin chlorid changes its density as the temperature rises, until 900° is reached, when it becomes constant at very nearly 94.27. This is nearly one-half of what it is at the temperature of volatilization, 606°. The other volatile compounds

of tin do not contain any smaller amount of the element, hence the amount of tin found in this molecule is the atom, and expresses its atomic mass. The student should show from these facts that the atomic mass is 117.8. What is the formula of the lower chlorid? As has just been pointed out, the two tin chlorids have densities of 94.27 and 129.64. The amount of tin in these molecules is exactly the same, and is taken as the mass of the atom. The amount of chlorin corresponds to two and four atoms of chlorin. Hence, tin has two degrees of valence. In the first case it is two, and four in the second. These facts agree with those found by a study of other compounds of tin. Tin, as to valence, is, therefore, represented thus, Sn^{II} and Sn^{IV}.

The atomic mass of tin as determined by a study of its volatile compounds is confirmed by the facts found in connection with its specific heat. Its specific heat is .54. (Determine atomic mass by facts given on page 63.)

Uses. — Owing to the properties of tin, which were brought out in the last study, it serves many useful purposes. Its alloys, with copper and zinc, constitute the bronzes. These bronzes vary in color, hardness, and physical properties, generally according to the relative proportions of copper, tin, and zinc. English bronze coins contain 95 per cent of copper, 4 per cent of tin, and 1 per cent of zinc. The more copper there is present in the alloy, the more distinctly yellow it is. The tin renders the alloy harder and more elastic. Alloys of copper and tin are also numerous, and vary in properties according to the relative proportions of the two elements. The more tin there is present in the alloy, the whiter it is. When the proportions are 66.34 per cent of copper and 33.33 per cent of tin, the alloy is called speculum metal and is capable of taking a brilliant polish. It is used for making reflecting mirrors for telescopes. Gun-metal, which contains 90.5 per cent of copper and 9.5 per cent of tin, is very hard and tena-

cious. The alloys of tin and lead have been referred to as solder. Another alloy, known as type-metal, consists of 25 per cent of each tin and antimony and 50 per cent of lead.

Another use of tin growing out of its chemical properties is that of a covering for useful utensils made of sheet iron or of copper. The surface of the metal is made free from oxids and dipped in the molten tin. If the metal is properly coated with tin, it will, for most purposes, last longer than it would if it were made of pure tin. The two metals, iron and copper, are harder and stronger than tin, and at the same time, being more abundant, are cheaper.

The iron is coated by first making the surface thoroughly clean by scouring and washing in acids, alkalis, and water. Tin is then melted in deep vessels, into which the sheets of iron are dipped, removed, and drained. This operation may be repeated several times, and each time a new layer of tin is added to the iron. The surface of the molten tin is covered with tallow to prevent the iron from becoming oxidized as it becomes heated.

Lead is often used with the tin for coating the iron, and such a plate is known as terne-plate. It is used for covering roofs and for similar purposes. Such plate cannot be safely used for making cooking or canning vessels, since the lead forms soluble salts with the acids and other substances found in the foods, and the latter is thus rendered poisonous. Water also acts upon such an alloy, and thus vessels made of such tin-plate should not be used for ordinary culinary purposes.

The amalgam of tin is used for the reflecting surface of mirrors. The glass properly cleaned is covered with tin-foil, and mercury is brought in contact with it, when it rapidly spreads through the foil. The excess of mercury is squeezed out by pressure, which brings the amalgam in close contact with the glass, thus forming a plane reflecting surface.

Experimental Study, No. 11. — Use a solution of each of the chlorids and make a parallel study.

(*a*) Use the usual reagents. Arrange facts of solubility thus determined in the table, and write the reactions. The alkali carbonates precipitate the hydroxids in each case. Note the facts in reference to excess of reagents. Stannic salts produce the oxy-phosphate ($Sn_2O(PO_4)_2$).

(*b*) Filter out the sulfids, and treat portions of each with yellow ammonium sulfid and warm gently. Compare with the action of these reagents on sulfids of arsenic and antimony. (The compound is $(NH_4)_2SnS_3$ in both cases, provided the yellow sulfid of ammonia is used. Stannous sulfid is only slightly soluble in the colorless ammonium sulfid.) Add a few drops of acid to the solution. Note that stannic sulfid is precipitated in both cases. Compare with arsenic and antimony.

To a portion of each of the sulfids add fairly concentrated hydrochloric acid and heat; what gas escapes? In what combination is the tin? Write the reactions. To the solution thus prepared add a piece of zinc and allow the action to proceed for some time. Prove what the black precipitate is by filtering it out and washing it until it gives no test for hydrogen chlorid. Dissolve it in hydrochloric acid, and to a portion (slightly acid) add hydrogen sulfid. To another portion add a few drops of chlorin water and boil until all of the free chlorin is driven off. Now pass in hydrogen sulfid. What do these results show? What produced the change? Suppose arsenic and antimony compounds had been present in the solution of the tin salt, what changes would have been produced in them by this treatment?

(*c*) Repeat (*f*) Experimental Study, No. 6, under MERCURY. Filter out the precipitate and add hydrogen sulfid. Explain.

(*d*) To a solution of stannic chlorid add powdered tin and boil for some time. Test a portion of the solution with hydrogen sulfid. What change has been made in the tin compound? Explain and write the reaction. What is such an action called? What are the agents?

(*e*) Into an acid solution of stannous chlorid pass sulfur dioxid until saturated. Boil to drive off excess. Prove whether the tin is "ic" or "ous." What kind of agent is sulfur dioxid usually? Explain action here.

(*f*) Heat on charcoal a mixture of a tin compound (SnO_2), sodium carbonate, and borax. Explain use of each reagent.

(*g*) To an acid solution (HCl) of stannous chlorid add a solution of ferric chlorid ($FeCl_3$). Warm and add potassium ferricyanid ($K_3Fe(CN)_6$). Note the color of the precipitate, — a delicate test for "ous" tin, providing there is no other reducing agent present. (See under IRON.) What change has occurred in the iron compound? Test some of the original solution of the ferric chlorid with $K_3Fe(CN)_6$.

(*h*) To a solution of stannic chlorid add calcium carbonate, not in excess. Filter out the gelatinous precipitate and wash thoroughly. Test the residue with litmus paper. (This compound, when carefully dried over sulfuric acid, is found to have the composition represented by the formula H_2SnO_3.) Wash this precipitate in a beaker, and warm, adding, drop by drop, a solution of potassium hydroxid until the mass is dissolved. Concentrate the solution to crystallization. What is the reaction?

(*i*) Treat some tin with concentrated nitric acid, and heat until the tin is wholly changed. Filter out the solid, wash, and treat as in (*h*). Concentrate the filtrate and test for ammonia. Explain the source of the ammonia. Write the reaction by which it was produced, considering the tin changed to metastannic acid ($H_{10}Sn_5O_{15}$).

Compounds of Tin.

General Statement. — Tin forms two classes of compounds, corresponding to its variable valence of two and four, which are distinguished as stannous and stannic compounds.

Tin in its "ous" condition is basic, while in its "ic" condition it is either basic or acid, according to the conditions under which it exists. These compounds are quite readily decomposed. The acid characteristic, however, is the most marked. The two principal classes of compounds corresponding with the acid tin are called the stannates and metastannates.

The stannous compounds are readily changed to the stannic form, and are consequently good reducing agents. The stannic compounds are not readily changed to the "ous" form, and hence are not good oxidizing agents. Metallic tin aided by heat does produce this change. Copper and zinc also set the metal free.

(*a*) **The Oxids and Hydroxids.** — As has been seen, the element tin does not readily unite with oxygen except at high temperatures; but the lower oxid (SnO) readily becomes stannic oxid (SnO_2). Oxidizing agents, like nitric acid, convert tin directly into stannic oxid, or hydrated compounds corresponding to it, without first producing the lower oxid, as is the case with mercury, antimony, etc. From the compound formed the oxid is produced by driving off the water. The element has such an affinity for oxygen at high temperatures that it decomposes water vapor, forming the stannic oxid and hydrogen.

Stannous oxid is usually prepared from stannous chlorid by the action of the fixed alkalis or their carbonates. The insoluble hydroxid is produced at first, and from this the oxid is prepared by drying in the presence of nitrogen or carbon dioxid. This oxid is converted into the higher oxid by heating in the air, or by oxidizing agents. There are at least four hydroxids that have been produced and separated. These are the two normal hydroxids ($Sn(OH)_2$) and ($Sn(OH)_4$), produced by the action of the alkali hydroxid and carbonates on soluble tin salts (the chlorids), and two others produced as described in (*h*) and (*i*), Study No. 10, or by carefully adding an acid to

sodium stannate or metastannate. They are represented by the formulæ $(OH)_2SnO$ and $(HO)_2H_8Sn_3O_{16}$, respectively. All these hydroxids are decomposed by heat into water and stannic oxid. The latter two hydroxids are known as stannic and metastannic acids. The normal hydroxid ($Sn(OH)_4$) breaks up at boiling temperature into water and H_2SnO_3, or $(HO)_2SnO$.

(*b*) **Salts of Tin.** — Stannous chlorid ($SnCl_2$) (crystals, $SnCl_2.2\,H_2O$).

The method for the preparation of this compound has already been given. It dissolves in a small amount of pure water to a clear solution, but with much water an oxy-salt is formed having the formula $SnOHCl.H_2O$. The reaction is

$$SnCl_2 + 2\,H_2O = SnOHCl.H_2O + HCl.$$

If there is present in the water an amount of hydrogen chlorid greater than is shown by this reaction, the change does not occur. Consequently this basic salt is dissolved by hydrochloric acid. Oxygen dissolved in the water (or the solution standing in contact with the air) produces this basic salt. Metallic tin in the acid solution prevents the oxidation almost completely.

Stannous chlorid is a powerful reducing agent, as has been shown in (*c*), (*e*), and (*g*) of Study No. 10. It separates gold from its soluble salts. Under the name of tin salts it is used as a mordant in calico-printing and in dyeing.

Metallic tin and hydrogen chlorid are still more powerful in their reducing action, since the nascent hydrogen set free by the formation of the chlorid acts at the same time as a reducing agent.

Stannic Chlorid ($SnCl_4$). — Stannic chlorid is formed from stannous chlorid by the action of chlorin and by oxidizing agents in presence of hydrogen chlorid. It is also produced when chlorin acts on the element tin when the latter is in a

molten state. Tin, dissolved in aqua regia at a moderate temperature, is left in solution as stannic chlorid. The pure chlorid is a liquid boiling without decomposition at 113.9°. The liquid is decomposed by water, forming stannic hydroxid. The liquid fumes in the air owing to its attraction for the moisture present. It is soluble in water containing hydrogen chlorid. The acid character of the chlorid is shown by its power to absorb ammonium, forming the compound $SnCl_4.2\,NH_3$. It also unites with other chlorids, forming compounds that are permanent and that correspond to the stannates, the oxygen of which is replaced by chlorin. These chlorids unite in the proportion of two molecules of this salt to one molecule of the stannic chlorid. The new molecule formed with ammonium chlorid is $(NH_4)_2SnCl_6(Na_2SnO_3)$. This salt, called pink salt, is used in dyeing, since in dilute solution it is decomposed by heat into $SnO—(OH)_2$, stannic hydroxid, which unites with coloring-matter to form a permanent compound. It is consequently used in calico-printing. The alkali chlorids form similar compounds, and represent the best known of such compounds. Stannous chlorid also forms similar chlorids in which four atoms of chlorin furnish four units of valence, which are saturated by one atom of tin, satisfying two of the units, while the other two are supplied by the alkaline base, *e.g.* K_2SnCl_4.

Sulfids of Tin. — As has been often pointed out, sulfur acts chemically in a manner similar to oxygen, and often takes its place in compounds. Sulfur forms two compounds with tin, corresponding to the two oxids; namely, SnS and SnS_2. They are insoluble, and therefore may be formed by acting on a soluble salt of tin (chlorids) with hydrogen sulfid. Stannous sulfid is also produced by heating sulfur and tin together. The stannous sulfid is blackish brown in color, and is soluble in concentrated hydrochloric acid and in yellow ammonium sulfid. The acid forms stannous chlorid ($SnCl_2$), and sets hydrogen sulfid free. The ammonium sulfid forms sulfostan-

nates of the form $(NH_4)_2SnS_3$, corresponding with the stannates, Na_2SnO_3. These sulfostannates are decomposed by acids, forming the stannic sulfid. (Compare with the stannates under same conditions.)

Stannic sulfid is acted upon by the agents just mentioned, and in a similar manner, except, of course, that the tin is in the "ic" condition in all the compounds.

Another variety of stannic sulfid is produced by heating together tin amalgam, ammonium chlorid, and sulfur. A portion of the sulfid is vaporized, and is crystallized in the cool parts of the vessel in the form of gold-colored scales. This sulfid is insoluble in hydrochloric acid. It is used as a pigment in bronzing, and is known as mosaic gold.

Other Salts of Tin. — The nitrate and sulfate of tin have been prepared by the action of these acids on the hydroxid at low temperatures, but they are of interest only as possible chemical compounds. Most of the other salts are insoluble in water, and can be produced from the soluble chlorids by precipitation. These are the phosphates, oxalates, and iodids.

Stannates and Metastannates. — These compounds are salts of stannic and metastannic acids, H_2SnO_3 and $H_2.H_8Sn_5 - O_{15}$ (somewhat variable in composition). The salts of most importance are the sodium and potassium stannates and metastannates. Their method of formation has been given. Sodium stannate is prepared in large quantities, and is used in calico-printing. The alkali stannates are soluble in water, from which solution they crystallize with three molecules of water, *e.g.* $Na_2SnO_3.3\,H_2O$. The commercial article is made by fusing tin with sodium nitrate and sodium hydroxid.

BISMUTH.

Occurrence and Distribution. — Bismuth is not widely distributed in nature. The principal localities in which it is found

are in Saxony and in England. It occurs free and combined, but chiefly as the sulfid, bismuthanite, and the oxid, bismite. It is also found as the carbonate. The free metal is found in veins traversing granite, gneiss, and clay slate.

Preparation. — The native bismuth is often freed from some of its impurities by placing it in an inclined iron retort, which is heated in a furnace. The bismuth fuses and runs down the retort and is drawn off. By this method metallic impurities are left in the bismuth, and only a portion of the bismuth is extracted from the ore. It is more commonly extracted after the ore has been broken up and roasted by adding to it carbon, lime, and often iron, and heating in appropriate vessels. The roasting removes any of the volatile metals like arsenic. For many of the uses of the compounds of the metal it is required that the metal from which they are prepared should be very pure, especially that it be free from any poisonous metals, such as arsenic. This purity is secured by dissolving the impure metal in nitric acid, decomposing the nitrate thus formed by heating and reducing the oxid produced with charcoal. The metal is sometimes fused with potassium nitrate, which oxidizes the arsenic and some of the bismuth, leaving the remainder of the metal quite pure.

The sulfid ore is roasted and heated with carbon and lime, as has just been given for the native metal.

Experimental Study, No. 12. — (*a*) Examine a piece of bismuth for its physical properties.

(*b*) Close one end of a piece of glass tubing about 5 cm. long, heat, and pour in melted bismuth. Now allow it to cool. Note and explain the effect on the tube. Save, and return the bismuth.

(*c*) Melt together, in a crucible, 2 g. of each lead and tin with 4 g. of bismuth. When well fused together, pour upon an iron plate, and when cool, examine its physical properties, and compare with each of the metals of which it is composed.

Place a portion of the alloy in a test-tube and add 15 cc. of water; carefully heat to boiling-point. Determine the temperature at which the alloy melts.

(*d*) Slowly heat a piece of the bismuth in the air. Heat the iron spoon red hot and drop in the powdered metal. What facts are illustrated?

(*e*) Place a few crystals of iodin in a mortar and add powdered bismuth. Rub them together gently with the pestle. From this result what can be inferred about the action of chlorin and bromin on bismuth? Would the action be more rapid than it is with iodin? Why?

(*f*) Mix thoroughly in a test-tube and heat about equal volumes of bismuth and sulfur. Remove the product; powder, and heat with dilute nitric acid. Note what gases escape. Explain and write the reactions.

(*g*) Determine the action of the three acids upon the metal, and note the changes with dilute and concentrated acids, without and with the addition of heat. Save the solution in nitric acid for further study. What gas escapes when heated with sulfuric acid? Write the reaction in each case. Also use aqua regia. What is the product? Save this solution.

Physical Properties. — Bismuth is a heavy metal, standing next to silver, and has a specific gravity of 9.8. It is a brittle metal, and readily crystallizes when cooled from fusion. Its melting-point is between that of tin and lead, and is 267°. It resembles antimony in general appearance, but is characterized by a slightly reddish color. It alloys readily with many of the metals, such as lead, tin, and antimony. It volatilizes at about 1700°. Its specific heat is .0308.

Chemical Properties. — Bismuth is not readily attacked by oxygen at ordinary temperatures, but at red heat it unites with it very energetically, producing the oxid (Bi_2O_3). It unites readily with the halogens, forming stable compounds. The metal is not dissolved by hydrochloric acid nor by sulfuric

acid; it is only slowly attacked at high temperatures, forming sulfur dioxid and bismuth sulfate. Sulfur unites with the metal at high temperatures. Nitric acid readily dissolves it, with the usual products.

Name and History. — The element bismuth has been known since the fifteenth century. Mention of a substance that was probably bismuth is found in the writings of the earlier chemists. It was called bisemutum or wisemuth. It was quite completely described by Pott in 1539. The metal was often confounded with antimony during the period of the iatrochemists.

Atomic Mass and Valence. — Three volatile compounds of bismuth are known; namely, the chlorid, fluorid, and methid. According to the methods already given, the atomic mass of bismuth is 207.5, and the formulæ for the compounds mentioned are $BiCl_3$, BiF_3—$Bi(CH_3)_3$. This number 207.5 also agrees with that determined by the method of specific heat, and agrees with the results of the analysis and synthesis of the other compounds of the metal. According to the formulæ of the three compounds referred to, the valence of this element is three, or the element is trivalent. In reference to oxygen it is both trivalent and quinquivalent.

Uses. — The principal uses of bismuth depend upon the remarkable properties that it imparts to its alloys. As a metal its brittleness renders it unfit for most uses. The volume of the solid metal is measurably greater than that of the same mass of the molten metal, and it imparts this property to its alloys and also hardness. It also lowers the melting-point of alloys below that of any of their constituents. For example: an alloy of one part of each, tin and cadmium, two parts of lead, and four parts of bismuth, fuses at 60°. This is known as Wood's metal. Rose's metal contains one part each of tin and lead, and two parts of bismuth, and fuses at 94°. Similar alloys are used in stereotyping and for casts, and are often employed

in other ways in the printer's art. The alloys being strong and resistant at lower temperatures, are used as safety plugs for boilers and fire apparatus. When the temperature of the boiler rises above the temperature that is considered safe, these plugs soften and are forced out. The temperature of fusion of these alloys is regulated by varying the proportions of the metals out of which they are formed. These alloys are also used for soldering where low temperatures must be used.

Compounds of Bismuth.

Bismuth is a true metal in most of its properties. Its higher oxid, however, acts as an acid-forming oxid. These latter compounds are not yet well known. The principal compounds contain bismuth in the triad condition.

Experimental Study, No. 13. — (*a*) Heat some powdered bismuth for some time in air. Transfer a portion of the product to a test-tube and add a little water and boil. Note the solubility. Add hydrochloric acid and warm. Treat another portion of the oxid with nitric acid. What is the formula for this oxid and the salts formed? Write reactions.

(*b*) Use a solution of either the chlorid or nitrate, and add the usual reagents to portions of the solution. Write the reactions in each case, and note the solubility of the compounds, color, etc. Carbonates produce the basic salt, $Bi_2O_2CO_3$. Chromates precipitate the basic chromate, $Bi_2O(CrO_4)_2$.

(*c*) To a solution of stannous chlorid add NaOH until the precipitate formed is just dissolved. To this solution add a solution of a bismuth salt; Bi_2O_2 is formed. This is a delicate test for bismuth, or, on the other hand, for tin compounds. The solution must be kept alkaline. The reactions are —

$$SnCl_2 + 4\,NaOH = Na_2SnO_2 + 2\,NaCl + 2\,H_2O.$$

$$Na_2SnO_2 + 6\,NaOH + 2\,BiCl_3 = Na_2SnO_3 + 6\,NaCl + Bi_2O_2 + 3\,H_2O.$$

Filter out the black oxid, dry it, and heat in the air. Explain changes. To a portion of the filtrate add hydrochloric acid to slight acidity, and pass into it hydrogen sulfid. Write the reactions and explain.

(*d*) To a solution of bismuth chlorid add water slowly as long as a precipitate is formed. Filter out this precipitate, and to a portion of the filtrate add ammonia to neutralize nearly all of the free acid. Now add more water. With another portion of the filtrate make the test given in (*c*). What does this prove? Is all the bismuth removed? Add hydrochloric acid to some of the precipitate produced at first. Add water again. The compound formed with the water has the formula BiOCl. With the nitrate a variety of combinations occur, among which are $BiONO_3.H_2O$; $Bi_4O_5(NO_3)_2.H_2O$. (The chlorid should contain only just enough free acid to prevent precipitation. It can be made by adding to bismuth carbonate or to the oxid hydrochloric acid as long as any is dissolved. Filter if necessary.)

(*e*) To a solution of a bismuth salt add a piece of zinc (or iron, tin, or lead). Prove that the deposit is bismuth.

(*f*) Filter out and wash the sulfid produced in (*a*), and treat different portions with ammonium sulfid, hydrochloric acid, and with nitric acid. Note the results in each case. Neutralize the portion treated with nitric acid with ammonium hydroxid. Filter out the precipitate, and dissolve the precipitate in a little acid, and test by (*c*).

(*g*) Prepare some bismuth hydroxid ($Bi(OH)_3$). Filter it out and wash it. The hydroxid is now placed in a concentrated solution of sodium hydroxid, and chlorin gas passed through the hot solution until the solution is saturated. Note changes in color of the oxid. What kind of an agent is free chlorin in presence of water? What is the use of the alkali? What is one of the products when chlorin acts in the presence of water? The precipitate is filtered out and washed and treated with dilute nitric acid until the solution is slightly acid.

$$Bi(OH)_3 + 2\,Cl + 3\,NaOH = 2\,NaCl + NaBiO_3 + 3\,H_2O.$$
$$NaBiO_3 + HNO_3 = NaNO_3 + HBiO_3.$$
$$2\,HBiO_3 = Bi_2O_5 + H_2O.$$

The residue has been found to be represented by the formula $HBiO_3$ or $HO-BiO_2$. This substance has very weak acid properties, and its alkali salts have been prepared. When this hydroxid is gently heated to about 100°, it is converted into bismuthic oxid (Bi_2O_5), a reddish brown powder. See reaction below. This oxid is quite readily broken up, forming the more stable tetroxid (Bi_2O_4 or BiO_2-BiO_2). The tetroxid by high heat loses oxygen and becomes the trioxid (Bi_2O_3).

The pentoxid is dissolved by hydrochloric acid, forming bismuth trichlorid and free chlorin. Explain and write the reaction.

Compounds of Bismuth.

(*a*) **Oxids and Hydroxids.** — The oxids of bismuth are insoluble in water. The trioxid and pentoxid (Bi_2O_3 and Bi_2O_5) are normally formed according to a valence of 3 and 5. The other oxids, Bi_2O_2 and Bi_2O_4, may be regarded in the same manner as were the corresponding oxids of nitrogen. Both oxids are readily changed to the normal trioxid. They may be represented structurally as follows: —

$$O=Bi^{III}-Bi^{III}=O \quad \text{and} \quad \begin{matrix} O \\ \diagdown \\ \diagup \\ O \end{matrix} Bi^{V}-Bi^{V} \begin{matrix} \diagup \\ \diagdown \\ \diagup \\ \diagdown \end{matrix} \begin{matrix} O \\ \\ \\ O \end{matrix}$$

The trioxid is usually prepared by heating the metal in the air, by decomposing the carbonate or nitrate or hydroxid by heat. It is a yellow powder soluble in acids.

The hydroxid is prepared by treating a soluble salt with a cold solution of an alkaline hydroxid. At boiling temperatures the bismuthyl hydroxid (BiO—OH) is formed. The group

(BiO), bismuthyl, is an analogue to antimonyl (SbO), and produces salts of the same general form.

(*b*) **Salts.** — As has been pointed out, bismuth trioxid is decidedly basic and forms salts with most of the acids. Most of these salts are insoluble in water, and many of them are basic. The soluble salts are decomposed by water.

Bismuth Trichlorid ($BiCl_3$). — The trichlorid may be formed by the direct union of chlorin and bismuth. When thus formed, it is a granular white solid which takes up water (*i.e.* is deliquescent) when exposed to the air, and goes in solution. It resembles antimony trichlorid in this respect. It is easily fused, and at 435° is volatilized. The chlorid is also formed when the metal is dissolved in aqua regia, and also when its oxid, hydroxid, or carbonate are acted upon by hydrochloric acid. It is soluble in water, containing free hydrogen chlorid, but pure water decomposes it, forming the insoluble bismuthyl chlorid (oxy-chlorid), BiOCl. Evidently this action goes on until there is an equilibrium produced between the hydrogen chlorid and the bismuthyl chlorid, since if there is an excess of acid present, it prevents the formation of the latter compound. The weak basic character of the metal is shown by the fact that the chlorid takes up ammonia, forming such compounds as $BiCl_3 \cdot 3\,NH_3$.

The bismuthyl chlorid is known as "pearl powder" or "white," and is used as a cosmetic.

Each of the other halogens forms the tri-compounds, and that with fluorin is sufficiently stable to be volatilized.

Bismuth Nitrate Crystals ($Bi(NO_3)_3 \cdot 5\,H_2O$). — This salt is formed by the action of nitric acid on the metal or by the action of the same acid on the oxid, hydroxid, or carbonate. In its solubility it is like the trichlorid. Much water decomposes it, forming several basic nitrates, depending on the conditions under which they are formed; *i.e.* the concentration of the solution of the normal nitrate, the amount of free acid, and the temperature of the solution.

Bismuthyl nitrate ($BiONO_3$) is one of these compounds. Others are represented by the formulæ $NO_3-Bi\begin{matrix}OH\\OH\end{matrix}$ and $Bi\begin{matrix}OH\\(NO_3)_2\end{matrix}$. The former compound is much used in medicine under the name of bismuth subnitrate. It is used as a cosmetic and in glazing porcelain. The subnitrate used in medicine requires to be made according to special directions, in order to insure constancy of composition. (See *United States Pharmacopœia.*)

None of the oxy-salts are soluble in tartaric acid, which fact serves to separate and distinguish them from the oxy-salts of antimony, which are thus soluble.

Other Salts of Bismuth. — There are at least two sulfates of this metal. The normal salt has the formula $Bi_2(SO_4)_3$, and the basic salt is $(BiO)_2SO_4$. They are made by the action of dilute sulfuric acid on either the oxid, hydroxid, or carbonate. The *sulfid* (Bi_2S_3) occurs in nature, and is produced by precipitation and by heating sulfur and bismuth together. It is insoluble in water and in ammonium sulfid. (Compare arsenic, antimony, and tin sulfids.) It is soluble in nitric acid. Bismuth basic chromate ($Bi_2O(CrO_4)_2$) is a yellow compound resembling lead chromate in general appearance, but is distinguished from it by its insolubility in fixed alkali hydroxids.

COPPER.

Occurrence and Distribution. — Copper is widely distributed in nature in both the free and in the combined condition.

In the free condition, the deposits of copper are nearly pure, and are sometimes found crystallized, but it is usually amorphous. The largest masses of native copper are found in the Lake Superior region. Here masses of nearly pure copper have

been found weighing more than 400 tons. The veins of copper found here are often more than two feet in thickness. Native copper is also found in China, Japan, and other countries. Combined copper occurs principally as the oxids and sulfids of the metal. The basic carbonate is also found in quite large quantities in Australia. The principal sources of copper are the sulfids, chalcocites (Cu_2S), and chalcopyrites ($CuF.S_2$). The two oxids, Cu_2O, CuO, called the red copper ore, and the black copper (or cuprite and melaconite), are found in considerable quantities in the Ural Mountain region. The carbonate ores are known as malachite and azurite, the green and blue basic carbonates, $CuCO_3.Cu(OH)_2$ and $2\,CuCO_3Cu(OH)_2$.

Preparation. — The separation of copper from its ores constitutes one of the most extensive industries in the world, coming very near to that of iron in its importance. The essentials of the method of separation vary with the ore from which the copper is produced. If the ore is one of the oxids, the process is a very simple one, since carbon readily removes the oxygen at red heat. Such an ore is heated with carbon in the proper furnace, and the copper is set free and melted and drawn off. The basic carbonate ores also easily yield metallic copper. When these latter ores are heated, they are decomposed at a comparatively low temperature. Carbon dioxid and water are given off, leaving copper oxid, which is decomposed by carbon, as just stated. The two classes of ore are not pure unmixed compounds, but, like the ores of most of the other metals, contain impurities. Accordingly, slag material or a flux is added to remove these substances; but the metal so produced usually contains iron, arsenic, and often sulfur. This impure metal is fused in presence of air and a flux. These impurities are more readily oxidized than is the copper. The oxids produced escape as gas, or form a slag, which comes to the surface of the molten metal and is removed.

The greater part of the copper of commerce is produced

from its sulfid ores. Taking copper pyrites ($CuFeS_2$) as a typical ore, the process for obtaining the metal that suggests itself (taking into account the properties of the elements in the compound) is that of roasting the ore and then heating with an element that has great affinity for oxygen, like carbon or hydrogen, but this would leave most of the iron alloyed with the copper. In practice, it is found to be quite difficult to separate the copper from the iron and its other impurities, although the general process just described is the one commonly used to separate the copper. The process commonly used consists of some five to six steps, and in the final treatment but little carbon is necessary. The essentials of the process are the roasting of the ore by which a portion of the sulfur is oxidized and escapes as sulfur dioxid. Some of the iron is also oxidized.

This iron oxid and other impurities are removed by fusing the whole mass with a silicious fluxing material and some carbon. This forms with the oxid of iron a fusible iron silicate ($FeSiO_3$) mixed with other substances. In the first roasting the temperature is so regulated that but little of the copper sulfid is changed, while a large portion of the iron sulfid is oxidized. This operation may be repeated until the remaining mass is largely copper sulfid (Cu_2S). This is again roasted to remove sulfur and oxidize some of the copper. When this mass is fused, the copper oxid reacts with the sulfid in a manner similar to that of lead in the production of this metal from its sulfids; *e.g.* —

$$Cu_2S + 2\,CuO = 4\,Cu + SO_2.$$

The metal thus obtained still contains some impurities. It is finally fused again with a flux and some carbon, and the melted mass is stirred usually with green wood poles. The heat of the molten metal decomposes the compounds of wood, furnishing gases that aid in this final process.

The copper obtained by this process is rarely absolutely pure, and is not sufficiently pure for many industrial uses. For this purpose, copper is produced by the electrolytic process.

Experimental Study, No. 14.—(*a*) Examine a piece of copper for physical properties. Prepare rods of copper and iron of the same length and diameter, and attach to them, by means of wax, small nails or tacks at equal distances apart. Heat one end of each rod, and note conductibility of heat as to the fact and the relative rate of conduction.

(*b*) Heat a piece of bright sheet copper in the flame of the lamp, leaving the bright surface exposed to the air. Remove some of the scale thus formed. Of what must it be composed? Note the color of the lamp-flame. To what is it due? Produce sufficient of this scale, grind it up with carbon, and transfer it to a small ignition tube, and heat to bright red heat for some time. Explain the action and use of each substance. Write the reactions. (See pages 176 and 181, Part I.) What is the action of hydrogen on this oxid?

(*c*) Place a piece of bright iron (like a knife-blade) in a solution of copper sulfate. Is there any change in the material of the knife-blade? Rub off the deposit and examine the blade. Has it changed? Test the solution for iron. (See under IRON.)

(*d*) Place a globule of mercury on the bright surface of a piece of copper, and rub it around with the finger. Try to rub it off the surface. Place a piece of tin on a piece of sheet-copper on the ring of the retort-stand, cover it with ammonium chlorid, and heat to the fusion of the tin.

(*e*) Recall and study the action of the acids, the halogens, and sulfur on the metal as previously given. Write the reactions.

(*f*) Place a piece of copper in a dilute solution (4 to 5 per cent) of acetic acid (vinegar), and note the change when the copper is bright and when the surface is tarnished. Explain the results.

(*g*) Fill a test-tube with carbon dioxid, and place in the gas a bright and a tarnished piece of copper and a little water. Cork

up the tube and set it aside for twenty-four hours. Explain this action.

Physical Properties of Copper. — Copper is a very ductile, malleable, and tenacious metal, nearly as hard as pure iron. A wire 2 mm. in diameter requires a mass of 138 kg. to break it. It can be rolled into foil sufficiently thin to transmit a green light. The color of the metal is so characteristically red that other substances having a similar color are called copper-colored. It is heavier than iron, having a specific gravity of 8.8. It melts at a temperature of 1040° (*i.e.* about white heat), and is converted into a vapor at the high temperatures of the oxy-hydrogen flame. Commercial copper usually contains small amounts of several impurities such as arsenic, iron, silver, and lead. Pure copper is produced by electrolysis and by decomposing the pure oxid by hydrogen. Copper is, next to silver, the best conductor of electricity and heat. It alloys with many other metals, forming mixtures that are among the most useful alloys produced.

Chemical Properties. — Copper does not unite with pure oxygen at ordinary temperatures. In ordinary air it is attacked by the oxygen, forming a brown coating which usually becomes, in course of time, covered with a green basic carbonate. At high temperature, copper oxidizes readily in the air. It readily unites with halogens and with sulfur when it is finely divided and heated with them.

Nitric acid, either dilute or concentrated, dissolves copper, forming copper nitrate, nitric oxid (NO), and water, although the dilute acid requires heat to carry on the action. Concentrated sulfuric acid dissolves it by the aid of heat, as has been already explained in the study of sulfur dioxid. The action is also explained by regarding the reduction of the sulfuric acid as due to the direct action of the copper upon the action. (See under ZINC.)

Hydrochloric acid very slowly dissolves the metal. Copper

possesses the peculiar property of being acted upon by acids, if the metal has access to the air. Weak acids even, like acetic and carbonic acid, react with it if the metal is in contact with air; while, if the air is excluded from the pure metal, practically all acids, except nitric, do not attack it at ordinary temperatures. Alkalis also act on copper only in presence of the air. With the fixed alkalis the product is copper oxid (CuO). Ammonia in solution causes the copper to absorb oxygen quite rapidly, the oxid which is formed going into solution by the action of the ammonia. Nitrogen is prepared from air by this process.

Name and History. — The fact that copper occurs native in a nearly pure condition, and that it can be readily worked, places it among the metals that have been known from the earliest times. It was the first metal used by the early peoples. They made use of it for weapons of defence, and for tools and utensils of various kinds. It was the metal from which the alchemist derived support for his theories of transmutation of the ignoble metals into the noble metals. Nature supplied him with copper sulfate, into the solution of which he placed iron, and found that it was, as he thought, transmuted into copper.

The metal that was used by the Romans was obtained from the island of Cyprus, from which the element was called *aes cyprium*. The word *cyprium* in course of time became changed into *cuprum*, and from *cuprum* the word *copper* is derived. The symbol Cu is formed from *cuprum*.

Atomic Mass and Valence. — Copper forms but one compound, the vapor density of which has been determined. This is a compound of chlorin and copper. Its vapor density is 98.55, and consequently its molecular mass is 197.1. The compound consists of 64.109+ per cent of copper, and 35.891 per cent of chlorin. This shows that the molecule contains 70.74+ units of chlorin, and 126.36 units of copper. The amount of copper, therefore, corresponding to one atom of chlorin, and therefore to one atom of hydrogen, is 63.18 units.

Since but one volatile compound is known, this result does not determine whether this is one or more atoms of copper. The specific heat of copper is .095, which gives an atomic mass but little larger than 63.18. 63.18 parts of copper replace the two atoms of hydrogen in sulfuric acid to produce copperic sulfate. The two atoms are always replaced in the formation of this salt, indicating that no less quantity of copper can enter this molecule. Similar facts are found in considering other compounds of copper, and the atomic mass of this metal is fixed at 63.18. The formula for the chlorid just referred to is consequently Cu_2Cl_2. Two compounds of copper with chlorin are known; one, as we have seen, is represented by the formula Cu_2Cl_2. The other chlorid is made by subjecting the first one, cuprous chlorid, to the action of chlorin. The new compound contains one-half as much copper; *i.e.* for every 63.18 units of copper there are 70.74 units of chlorin. This shows that one atom of copper has replaced two atoms of hydrogen, or that copper acts as a dyad in this compound. In the first compound two atoms of copper are equivalent to two atoms of hydrogen, and the two atoms of copper are bivalent, or one atom is univalent. It is customary to regard copper as bivalent, and to explain the other chlorid by saying that one unit of valence of each atom of copper mutually satisfies the other, and that each of the other units is satisfied by chlorin. It is represented thus: —

$$\begin{matrix} Cu-Cl \\ | \\ Cu-Cl \end{matrix}, \text{ or } Cl-Cu-Cu-Cl.$$

There are two classes of salts, therefore, — one in which the group Cu_2 is bivalent, and one in which the atom replaces two atoms of hydrogen. The salts of one class can be made to pass into those of the other class by the proper agents, as will be seen in the next study. They are known as the cuprous and cupric classes of copper salts.

Uses of Copper. — The metal is one of the most useful metals. It is employed very largely in electrical appliances because of its cheapness and its great conducting power. In general, its physical and chemical properties make it useful in the construction of boilers, vessels for heating liquids, for covering iron, electrotyping, sheathing wooden ships, etc. It forms some of the most useful alloys with such metals as gold and silver, in coin and in jewelry; with zinc to form brass; with zinc and tin to form bronze; with zinc and nickel to form german silver, etc.

Compounds of Copper.

Experimental Study, No. 15. —(*a*) Heat a strip of copper in the upper part of the flame of the lamp, and while hot plunge the copper into water. Note the compound formed, as to color, etc. Next heat the copper so that the scale formed is either in the air or in the oxidizing flame. Note the changes and explain them. Give the formulæ for the two compounds.

(*b*) Dissolve some of the oxid formed (using about .5 g.) in hydrochloric acid, and evaporate the solution to dryness. Be careful and not overheat the residue. What is the compound? Write the reaction. Dissolve a portion of the residue in water for further study.

(*c*) Proceed in the same way, using dilute sulfuric acid. Redissolve in a little water, and allow it to crystallize. (Use evaporating-dish.)

(*d*) Treat 5 to 10 g. of copper with nitric acid, and warm until dissolved. Evaporate to dryness. (Do not overheat.) Take a portion of the residue, place it in a crucible, and heat to a high temperature. What is left? What has escaped? Explain and write reaction. What has been the effect of heating to a high temperature the nitrates already studied?

Given copper nitrate, how could you prepare copper chlorid or sulfate?

(*e*) To a solution of copper sulfate add NaOH in excess. Note precipitate, cupric hydroxid, and then boil the whole for a few minutes. What is the black residue? What has been the solubility of the hydroxids studied thus far, and what the effect of heat on them?

(*f*) To a solution of $CuSO_4$ slowly add ammonium hydroxid to saturation. Note changes. The action is characteristic of soluble copper compounds. The compound formed is $(NH_3)CuO.(NH_4)_2SO_4$. Add NaOH to the solution, and boil. The precipitate is CuO. Explain. Where is the ammonia?

(*g*) Use the reagents $K_3Fe(CN)_6$, $K_4Fe(CN)_6$.Na_2HPO_4, $(NH_4)_2C_2O_4$, and KCNS. The precipitates are normal, except that the phosphate may be either $CuHPO_4$ or $Cu_3(PO_4)_2$, according to which reagent is in excess. If the phosphate is in excess, the first-mentioned salt is formed.

(*h*) To a solution of the sulfate add a solution of fixed alkali carbonate; a basic carbonate is produced, $Cu(OH)_2.CuCO_3$. What gas escapes? Boil the mixture, using ammonium carbonate in excess.

(*i*) Pass hydrogen sulfid into a solution of copper sulfate (or add ammonium sulfid) as long as a precipitate is formed. Filter out, and wash the precipitate. Add to the residue on the filter paper hot moderately dilute nitric acid. To a portion of the filtrate add ammonium hydroxid to saturation. Write reactions. Suppose this had been an unknown substance and had given the results just produced, what could you assert as to the compound?

(*j*) Acidify, with hydrogen chlorid, a concentrated solution of cupric chlorid, and place it in a small Erlenmeyer flask, and add copper filings. Tightly stopper the flask, and let it stand for a day or two. More copper filings should be added if the

first addition disappears. Note changes in color of solution. After a day or so add water to a portion of the solution, and note change. What has become of the copper filings? To a portion of the solution add potassium iodid. Neutralize a portion of the acid if necessary to produce the reaction. Treat a solution of cupric chlorid with the potassium iodid solution. What produces the brown coloration? Prove it. Pass sulfur dioxid into the solution of cupric chlorid (or add sulfurous acid), and then add the solution of potassium iodid. Explain the difference between the two results. Filter out the precipitate, and test a portion of the filtrate for sulfuric acid. Place another portion of the solution in a flask, boil, and pass the steam into water. (This can be readily done by preparing the flask as it would be for making and collecting gas, and putting the end of the collecting-tube into a test-tube partly filled with water.) Add chlorin water to the distillate, and test with bisulfid of carbon. In what combination must the iodin have been? Write the reactions.

Pass air into the cuprous chlorid solution. Explain the change in the color of the solution. Make tests to show what the change is, using facts just learned. Write the reaction. This study shows what in reference to the two classes of copper compounds?

(*k*) To the solution of cuprous chlorid add a solution of stannous chlorid. Explain the results.

(*l*) To a solution of copper sulfate add sodium hydroxid in excess. To this add a solution of glucose until all the copper hydroxid is dissolved. Now boil the solution. Cu_2O is the precipitate. This oxid may be filtered out, and the actions of acids upon it determined.

(*m*) Make a borax bead, and fuse it with a small amount of cupric oxid. Heat this bead in the reducing flame for some time. In what condition is the copper now? Where is the oxygen?

(*n*) Make a water solution of the white of an egg; add it to a solution of a copper salt. Note the action. Add an excess of the egg solution, shake well, and let it stand for a short time, then filter out the precipitate, and test the filtrate for copper. (See (*f*).)

Compounds of Copper.

(*a*) **Oxids and Hydroxids.** — Copper forms two oxids having the composition indicated by its valence; namely, CuO and Cu_2O. Cuprous oxid (Cu_2O) is a bright red crystalline substance produced by the reduction of cupric sulfate by means of such organic substances as glucose. (A complete explanation of this reaction is not profitably given here.) The oxid is also produced by heating sheets of copper in a limited supply of air. It is sufficiently stable to be fused if not in contact with air. It can be fused with glass, imparting to it a red color. Cuprous oxid is decomposed by most acids (hydrochloric acid is an exception), cupric salts are formed and copper is set free, especially if the acids are dilute; *i.e.* copper is both reduced and oxidized. This oxid is soluble in ammonium hydroxid, and this solution rapidly takes oxygen from the air, changing the cuprous oxid to cupric oxid, which is soluble in ammonium hydroxid, forming a blue compound, the composition of which is not known.

Cupric oxid is prepared by heating copper in oxygen and by decomposing the nitrate, carbonate, or hydroxid by heat. The dark-colored coating formed on copper vessels by standing in the air is cupric oxid. It is this coating that is dissolved by the acid of fruits and other organic acids, forming soluble salts when such tarnished copper vessels are used in cooking.

This oxid is used in the quantitative analysis of organic compounds, since it yields its oxygen at red heat to the carbon and hydrogen of such compounds, forming carbon dioxid and water. These products are separately saved by the proper

reagents, and weighed, and from the results the amount of carbon and hydrogen can be calculated.

It is doubtful whether the normal cuprous hydroxid has been separated. It is so unstable that it soon decomposes into water and cuprous oxid if it is produced by precipitation. Cupric hydroxid is precipitated in the usual manner, but is unstable, and changes by heat to cupric oxid, forming several intermediate compounds containing less hydroxyl than the normal compound.

Ammonium hydroxid forms the cupric hydroxid when used in small amounts, but in excess of this reagent it dissolves, or soluble compounds are formed, in which ammonia (NH_3) is combined with the original salt, the compound being usually hydrated. (See under SALTS OF COPPER.) The solution formed is a brilliant blue in color. This is a delicate test for copper compounds, indicating 1 part of copper in 100,000 parts of a water solution.

There are two other oxids of copper that have been produced under special conditions. They are represented by the formulæ Cu_4O and CuO_2, called copper tetrantoxid (or suboxid) and peroxid or dioxid respectively. Copper tetrantoxid is produced by the reducing agent stannous chlorid in alkaline solutions, acting on cupric salts such as cupric sulfate. It is an olive-green powder that takes up oxygen when brought into the air, or when acted on by an oxidizing agent. The dioxid is a very unstable oxid, formed by the action of hydrogen dioxide on cupric hydroxid. It is doubtful whether it has been prepared free from water. The strongest reducing agents like hypophosphorous acid reduce copper salts, forming a hydrogen compound represented by the formula Cu_2H_2. It is very unstable and decomposes rapidly at about 50°.

(*b*) **Salts. — Cuprous Chlorid (Cu_2Cl_2).** — Cuprous chlorid is formed by several methods; *e.g.* by the action of chlorin on copper, by boiling cupric chlorid with finely divided copper,

and by the action of various reducing agents on the same chlorid. (See study.) It is a grayish white compound which is only slightly soluble in water, but is soluble in hydrochloric acid. It is volatile at about 1000°. It is soluble in ammonia, forming different compounds according to conditions; *e.g.* —

$$Cu_2Cl_2(NH_3)_2 \text{ and } 2(Cu_2Cl_2)(NH_3)_2.$$

The acid solution of the chlorid takes up oxygen from the air, forming the green basic cupric chlorid, OH—Cu—Cl.

Its hydrochloric acid solution also absorbs carbon monoxid and is used in gas analysis for this purpose.

Cupric Chlorid = $CuCl_2$. (Crystal $CuCl_2.2H_2O$). — Cupric chlorid is soluble in water, producing a green solution. It is quite stable, but at high heat decomposes into chlorin and cuprous chlorid. It unites with ammonia, forming such compounds as $CuCl_2.6NH_3$. It forms double salts with many other chlorids.

Iodin forms but one compound with copper; namely, cuprous iodid (Cu_2I_2). This compound is produced when a soluble cupric salt is treated with potassium iodid. The copper is reduced to the cuprous condition, and iodin is oxidized, it being set free.

The other cuprous salts are of but little interest except from the purely chemical standpoint. They are changed from one form to the other by the proper reducing or oxidizing agents.

Cupric Sulfate, Blue Vitriol, $CuSO_4$. (Crystals, $CuSO_4.5H_2O$). — Copper sulfate is the most useful salt of this metal. It is a soluble compound, and therefore cannot be prepared by precipitation. It is commonly made, commercially, by slowly roasting for some time at low heat cuprous sulfid (Cu_2S), thus forming copper sulfate. The roasted mass is treated with water, and the sulfate is dissolved out along with some impu-

rities. The solution is concentrated, and the salt crystallizes with 5 molecules of water of crystallization.[1]

The sulfate is also produced by the action of sulfuric acid on either the metal copper, or on its oxid, or on the carbonate. It has been previously stated that the action of sulfuric acid on copper is, that the hydrogen given off during the action reduces the sulfuric acid. These compounds, sulfur dioxid,

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[1] The water that is retained by the crystals of this and other salts is called the water of crystallization. This water is, in a certain sense, combined with the molecules of the salt, although it is held with different degrees of firmness in different crystals. Some of the characteristics of this water may be summarized as follows: —

(*a*) It enters the molecule when the salt is crystallized from solutions, the amount being constant within certain limits of temperature.

(*b*) The amount of water that is found in any given crystals depends on the temperature at which they are formed. At high temperatures, no water is included in the molecule, while at low temperatures the amount is increased. For example, ammonium chlorid forms crystals from solutions at ordinary temperatures that contain no water, while if the solution is at — 15°, crystals are produced that contain 12 H_2O.

(*c*) This water escapes from the crystals of different salts at a fairly constant temperature for the same substance, but at widely varying temperatures for different salts. By constant temperature is meant here one at which all of the water escapes, although a portion may escape at lower temperatures. For example, sodium sulfate crystallizes with ten molecules of water, but when the crystals are removed from the solution and exposed to the air, a portion of the water escapes, and the crystals are left as a fine powder. In the case of this salt, all of the water is not driven off until a temperature of 35° to 40° is reached.

(*d*) In many cases the water is in part driven off at about the boiling-point of water, while one or more molecules require in some cases low red heat before they are set free. This remaining portion is called water of constitution. For example, magnesium sulfate crystallizes with seven molecules of water, $MgSO_4 . 7\,H_2O$, but at 150° the salt loses six molecules of water. The last molecule requires a temperature of 200° before it is driven off. It is readily seen that the bond of affinity increases as the water is driven off. In case of sulfates, it is probable that the compounds become salts of the higher hydroxyl acids. (See page 223, Part I.) For magnesium, the salt is one of the tetrahydroxyl acids, $SO(OH)_4$.

Crystallized gypsum is probably a salt of hexahydroxyl sulfuric acid, $S(OH)_6$. (See under CALCIUM.)

copper sulfate, and water, constitute the main products. There are small amounts of other products. This is readily seen when copper is dissolved in sulfuric acid, since there is formed, especially at the beginning of the action, a brown to black insoluble compound. It is claimed by good authority that copper directly reduces sulfuric acid, and that it is not the hydrogen that produces the result. The salt crystallizes in beautiful blue crystals, which become grayish white when they are heated to 100° for some time. Four molecules of water are thus driven off. The fifth molecule is not set free until the salt is heated to a temperature of 200° and above.

The anhydrous salt has great attraction for water, regaining its blue color when water is added to it. The dry salt is often used as a desiccating substance.

Ammonia unites with copper sulfate, in proportions depending on the conditions imposed. For example, if the blue solution produced by adding ammonium hydroxid in excess to the sulfate solution is treated with alcohol, a crystalline compound separates out, which has the composition represented by the formula $CuSO_4.4\,NH_3.H_2O$. If this compound is heated to 150°, the water and two molecules of ammonia escape, leaving the compound $CuSO_4.2\,NH_3$. Just how this ammonia is combined in this compound is not wholly determined. It is often considered that a compound is formed, the conception of which is represented by the formula $Cu\begin{matrix}\diagup NH_3 \diagdown \\ \diagdown NH_3 \diagup\end{matrix}SO_4$. The acid group ($SO_4$) can be replaced by other acid groups.

Copper sulfate forms double salts with several other sulfates. These salts crystallize out of their mixed solution. The salt crystallizing with the copper sulfate is isomorphous with it; *e.g.*

$$FeSO_4.CuSO_4.7\,H_2O\,;\ (NH_4)_2SO_4.CuSO_4.6\,H_2O.$$

Copper sulfate is used as the source of other compounds of copper, such as Scheele's green ($CuHAsO_3$) and other pig-

ments. This is used in calico-printing, wall paper, etc. It is employed as an insecticide and as a preservative in a great variety of cases, such as the preserving of wood, etc. It is employed in gravity and other electric batteries, and in electroplating, the metallic copper being deposited on the negative pole, which is the object to be plated.

Cupric Nitrate ($Cu(NO_3)_2$) — (**Crystals** — $Cu(NO_3)_2.3H_2O$). —Cupric nitrate is produced by the action of nitric acid upon the metal, the oxid, the hydroxid, or the carbonate. It crystallizes in blue crystals which are deliquescent. It is easily decomposed by heat and by reducing agents, and is a powerful oxidizing agent, the copper being often left in the cuprous condition. It is used as an oxidizing agent in dyeing.

Cupric Carbonate. —Copper carbonate, as has been stated, occurs in nature in two forms, malachite and azurite. The former is produced when a soluble salt of copper is treated with a fixed alkali carbonate. The compound is a basic salt having the formula $CuCO_3.Cu(OH)_2$ or $\begin{matrix} HO-Cu-O \\ HO-Cu-O \end{matrix}\!\!>\!CO$.

Azurite is also a basic salt, $Cu(OH)_2.2\,CuCO_3$.

Copper left exposed to the air and water becomes covered with the malachite carbonate. The normal carbonate is not known.

Copper Sulfids. — Both cuprous and cupric sulfids are found in nature, although the principal one is cuprous sulfid. Both sulfids are formed by heating copper and sulfur together, the resulting compound depending on the proportions of sulfur to copper and the temperature used. If the temperature is much above 450°, only cuprous sulfid is formed. Cupric sulfid is formed by passing hydrogen sulfid into a solution of a copper salt. This black, moist precipitate is easily oxidized when exposed to the air, forming cupric sulfate. Cupric sulfid is slightly soluble in ammonium sulfid, and is readily soluble in nitric acid. Hydrogen removes one-half of the sulfur from this sulfid, forming cuprous sulfid (Cu_2S).

Native cupric sulfid is known as indigo copper, or covellite, and native cuprous sulfid as copper glance and chalcocite.

Other Salts of Copper. — The most of the other inorganic salts of copper have been prepared in the last experimental study.

The cyanids form double salts with potassium cyanid in excess of this reagent. This solution is used in electro-copper plating.

Cupric ferro-cyanid ($Cu_2Fe(CN)_6$) is of interest, since it is very insoluble, and a very dilute solution of a cupric salt is changed to a reddish color by the addition of potassium ferro-cyanid. This is a most delicate test for copper compounds in solution.

Paris green and Scheele's green are valuable salts of copper that are used as pigments. Paris green is a more or less impure cupric arsenite and acetate.

Copper compounds are quite poisonous, although less so than are those of lead, mercury, etc. Cases of poisoning from copper compounds are not uncommon, since vessels made of copper are used in many culinary and other manufacturing processes. The property of copper which renders it soluble in weak acids in presence of air makes it unfit for use in making cooking-vessels unless great care is used. When dilute solutions of such acids as acetic acid is left in contact with copper in the air, basic copper acetate is formed. This substance, which is called *vert-de-gris*, thus often gets into food. Many articles of food are colored a beautiful green by small quantities of copper salt, especially those whose appearance is considered to be more attractive when thus colored. Small quantities of copper salts produce chronic poisoning. The best antidote for acute poisoning with copper compounds is the white of an egg mixed with water. An insoluble compound is formed with the copper salts, which can be removed from the stomach by emetics.

CADMIUM.

Occurrence and Preparation. — Cadmium is one of the rare elements. It occurs in small quantities in many zinc ores, and also as a sulfid in the mineral greenockite. The amount present in the zinc ores varies from 1 to 5 per cent. In preparing zinc from its ores (see ZINC), the distillate that first comes from the retort contains the cadmium, since it is volatile at a lower temperature than zinc. (It boils at 860°, while zinc boils at 1040°.)

These first vapors are mostly oxidized, so that the product contains the oxids of both zinc and cadmium. These oxids are mixed with charcoal and heated in a closed retort, and the first of the distillate contains most of the cadmium. The more or less impure distillate is dissolved in hydrochloric acid, and this solution is then treated with a solution of ammonium carbonate. This reagent forms carbonates with the impurities present or leaves them in solution. The carbonates all dissolve in excess of the reagent except that of cadmium. This is separated, washed, and ignited with charcoal, and the pure metal distilled over. The principal impurities are zinc, copper, and arsenic.

Properties. — Cadmium is a metal resembling tin in many of its properties. It is a malleable, ductile, and quite soft metal. Its specific gravity varies from 8.5 to 8.6.

The metal is only slightly oxidized or changed in air at ordinary temperatures. At high temperatures it rapidly unites with oxygen, producing a brown oxid. It readily unites with the halogens and with sulfur. It is slowly dissolved by either dilute hydrochloric or sulfuric acids, and readily so in nitric acid, forming the corresponding salts.

Name, History, and Uses. — The word *cadmium* is derived from *cadmia* referring to its connection with zinc. It was discovered in 1817 by Stromeyer, and by Herrmann in 1819.

These two men published an account of their investigations of the metal and of many of its compounds. The metal is used in alloys, especially when alloyed with zinc, with which it forms a soft substance used in filling teeth. This alloy possesses the property of hardening very soon after its preparation.

Atomic Mass and Valence. — Two of the halogen compounds of cadmium, the chlorid and bromid, are volatile. A study of these compounds shows that 70.74 parts of chlorin and 159.6 parts of bromin each unite with 111.8 parts of cadmium. This is the number found for the atomic mass of the element by the method of specific heat. The specific heat is .054. It also agrees closely with the number found by analytical methods of study. It was found, for example, by the study of the bromid changing it into silver bromid, that if silver is 107.7, then cadmium is very close to the number given, 111.8. The formula for the halogens is of the form CdX_2. Cadmium is bivalent in all of its salts.

Compounds of Cadmium.

Experimental Study, No. 16. — (*a*) (Use a solution of cadmium sulfate or chlorid.) Treat this solution in the usual manner with the reagents, noting solubility, color, etc. Write the reactions. A basic carbonate of variable composition is formed by the fixed alkali carbonates. The other salts are normal. Filter out the sulfid and study its solubility in hydrochloric, in nitric, in dilute sulfuric acids, and in ammonium sulfid. Compare with the other sulfids. Strongly acidify (with HCl) a solution of a cadmium salt and pass hydrogen sulfid into the solution. Note the result and explain. Nearly neutralize the solution, yet leave it distinctly acid. Note and explain the result.

(*b*) Add to the cadmium salt a solution of potassium cyanid, slowly, and then in excess. A double salt is formed, —

$$2\,KCN.Cd(CN)_2 \text{ or } K_2Cd(CN)_4.$$

Treat a soluble salt of copper in the same manner;

$$2\,KCN.Cu(CN)_2$$

is formed. Pass hydrogen sulfid into each of the solutions. Note results for use in separating these two elements from each other.

(*c*) Heat some cadmium salt (sulfate) on charcoal. Explain the changes.

(*d*) Mix a cadmium compound (CdO) with carbon and heat it in an ignition tube. Write and explain the reactions.

(*e*) In a solution of cadmium salt place a piece of zinc or magnesium. Explain.

Cadmium is bivalent in all of its salts. The salts are formed in the usual manner. Cadmium sulfid is an insoluble brilliant yellow compound used as a pigment, especially in oil paintings. It is soluble in concentrated hydrochloric acid, but it is only slightly so in the dilute acid. It is insoluble in ammonium sulfid, the only yellow sulfid that is not soluble.

Cadmium cyanid is soluble in potassium cyanid, forming the double salt, $(KCN)_2Cd(CN)_2$. Hydrogen sulfid decomposes this compound, forming cadmium sulfid. Copper forms a similar double cyanid, but hydrogen sulfid does not decompose it to form copper sulfid. This fact is made use of in separating copper from cadmium when their soluble compounds are mixed.

GOLD.

Occurrence and Distribution. — Gold is widely distributed, although generally in small quantities. It is generally found free, although it is found combined with tellurium and with silver and tellurium. This mineral, called sylvanite, is found in

California and in Austria. The native gold is found in alluvial deposits and in veins of quartz that pass through metamorphosed rock. The principal localities for native gold are in California, Siberia, Australia, Mexico, and the Ural Mountains. Gold is also found in most silver and lead ores and in iron pyrites. Sea-water contains a small amount.

Preparation. — The native gold found in alluvial deposits is usually in the form of small pieces often so finely divided as to be called "dust" or "scale." The larger pieces, called nuggets, are rare and are not often more than a few grammes in mass, although nuggets have been found weighing 90 kg. It occurs also in the crystalline form, usually as octahedra. and dodecahedra.

The process of extraction is generally quite simple and is mostly mechanical in character. The alluvial deposits are washed by running water, the current being sufficiently strong to carry off the lighter particles of sand, etc., leaving the heavier gold and some other material behind. This residue is now transferred to the proper vessels and shaken well with an excess of mercury. The gold amalgamates with the mercury and is thus separated from its mechanical impurities. The excess of mercury is removed by pressure and the remainder by distillation. This whole process is called placer mining. The gold that is found in quartz veins is removed by a process similar to that just described. The quartz rock is crushed to a fine powder, and this is treated with water and mercury. Placer mining is now often modified by forcing water against old alluvial deposits, which are thus washed away. In this manner immense deposits of soil, etc., can be worked over, and although a given mass contains but little gold, the amount that can be moved makes the process profitable.

Native gold is not usually pure, but contains silver, and often iron, palladium, rhodium, copper, and platinum. Silver and copper are the most common impurities, and some assert that

silver is always found with the native gold. Crystals of gold have been found that contain as high as 38 per cent of silver. The amount of silver is usually less than 10 per cent. The other impurities vary from a trace to small, but measurable, amounts. The silver is removed by any one of several processes.

The native gold is dissolved in aqua regia and evaporated to expel the excess of the nitric acid, and hydrochloric acid is added (if necessary) to precipitate the silver chlorid. The chlorid is filtered out, and the gold is set free from its compound ($CuCl_3$) as a fine powder by reducing agents such as another metal (zinc), but more commonly by ferrous sulfate or oxalic acid (which see). The last two reducing agents do not reduce the other metals that may be present. The metal is fused and made into ingots. Another method depends on the notable fact that, although both nitric and sulfuric acids dissolve free silver (but do not attack gold), they will not remove all the metal from the alloy if it contains more than about 25 per cent of gold. An alloy richer than this is fused with sufficient silver to reduce the quantity of gold to about this amount, *i.e.* to one-fourth. The process is called quartation. Gold is also obtained in quite large quantities according to the method given under Parkes' process, from silver bullion which has been produced from ores that contain but a small per cent of gold. The lead and silver are separated by the modified Parkes' process (which see).

The properties of gold render it one of the most useful of the metals. It is the most ductile and malleable of all the metals. It may be hammered into sheets which are only $\frac{1}{282000}$ inch in thickness. These sheets transmit a greenish light. An ounce of gold will make a sheet having an area of 189 square feet. It can be drawn into wire so fine that one ounce will form a wire 6620 miles long. It is a good conductor of heat and electricity. In a finely divided condition, gold is of a reddish

violet color when suspended in water. This property of gold is taken advantage of in making glass by adding to the molten glass a very small amount of finely divided gold. Gold fuses at about 1250°, and is volatilized to a slight extent at the highest temperatures. Its specific gravity is 19.3.

Chemical Properties. — Gold is chemically a very inert element. It is not attacked by the air at any temperatures and resists the solvent action of all the acids (except selenic acid) and also of the alkalis. It unites directly with the halogens at raised temperatures, and with nascent chlorin very readily, forming the corresponding binary compound. It is, therefore, soluble in aqua regia. It is not acted upon by hydrogen sulfid and does not unite directly with sulfur. Gold is, therefore, a weak base, and in combination with chlorin forms a group that is acidic. The compound is represented by the formula $HAuCl_4$ chlorauric acid, which forms salts with the stronger bases, like potassium ($KAuCl_4$), which is called potassium chloraurate.

Name and History. — Owing to the fact that gold occurs free in nature and is widely distributed, it has been known from the earliest times. Its properties of softness, malleability, and ductility made it one of the most highly prized of all the metals known to the ancients, without regard to the natural supply. It could be readily shaped into attractive forms, and at the same time its unchangeability and beauty made it the most sought after of natural substances. The symbol Au is derived from the word *aurum*, which refers to its yellow color. The word *gold* is of ancient origin, and also refers to color.

Atomic or Combining Mass and Valence. — Gold forms no known compounds that are volatile, and hence no aid to the determination of its atomic mass can be had by a study of such compounds.

The method using specific heat gives the number as 196.7. The analytical methods give a number very near this, and 196

is taken as the atomic mass, or better in this case, its combining number. 196.2 parts of gold unite with 106.11 parts of chlorin or with 3 atoms of chlorin. If this fact and similar ones are considered as determining valence, then gold is trivalent.

It forms another compound with chlorin, in which 196.2 parts of gold are united with 35.37 parts of chlorin, and therefore it is sometimes univalent. These two classes of compounds are known and are distinguished in the usual way, *i.e.* as aurous and auric compounds.

Uses of Gold. — Gold forms many useful alloys, especially with copper, mercury, and silver. Its alloy with copper is used for coin and in making works of art and for ornamentation. Copper makes the alloy harder than the pure gold, which is too soft for most uses. In coins of the United States, 10 parts (or 10 per cent) of copper are alloyed with 90 parts (90 per cent) of gold. English coins contain 91.66 per cent of gold. The gold used in the arts contains varying amounts of the pure metal. The proportion of gold in its alloy with copper is indicated by the word *carat*. Any given amount of the alloy may be considered as divided into 24 parts, each one of which is a carat. If the gold is pure, it is spoken of as 24 carat fine. If one-half is gold, then it is 12 carat fine, etc., or it contains 12 parts of gold and 12 parts of copper. The amount of copper affects the color of the alloy; the more copper there is present in a given sample, the nearer a copper red it becomes. The alloys commonly in use are 18, 14, and 10 carat fine. English coin is 22 carat fine, and American coin is 21.6 carats. Silver forms alloys that are yellow white to nearly white in color, depending on the relative amount of the gold and the silver. Mercury alloys (amalgams) are often used for gilding. The alloy is spread on the surface of the metal to be gilded. This is afterwards heated until the mercury is driven off, leaving a thin coating of gold. Gold is also applied to wood, leather, and similar substances in the form

of gold-foil held in place by varnish or glue. Earthenware is gilded by mixing finely divided gold in oil of turpentine and applying to the surface. This ware is afterwards heated until fusion occurs. Gold is much used to plate or cover the surface of metals that are readily attacked by the air or other chemical agents, or that do not have the attractive appearance of gold. This gold coating or gilding is added to metallic substances by connecting the body to be covered with the negative pole of a current of electricity, while to the other pole is attached a rod of gold. The two poles are now immersed in a solution of the double cyanid of gold and potassium, $KCN.Au(CN)_3$.

Compounds of Gold.

Gold does not form many stable compounds. The principal ones are the halogen compounds, the oxids and sulfids. There are some double salts, to which reference has already been made.

Gold trichlorid is made by the action of nascent chlorin on gold as produced in aqua regia. It can be produced in the crystalline form ($AuCl_3.2\,H_2O$) from this solution by evaporating to dryness and redissolving and crystallizing it. The trichlorid is decomposed at a temperature of about 190° into aurous chlorid and chlorin. Higher temperatures complete the decomposition. Reducing agents also produce the complete decomposition of this compound, and in fact other compounds of gold. Gold compounds are, therefore, powerful oxidizing agents. Stannous chlorid produces a purple precipitate with the trichlorid (called the purple of Cassius). The composition is not definitely known, but it is probably a gold and tin stannate. This pigment is used in decorating porcelain and chinaware, producing, when "baked," shades from pink to rose-red.

Gold cannot be made to unite directly with oxygen. The oxid is prepared indirectly by producing the hydroxid, and making this anhydrous by means of gentle heat. It is usually formed by adding an excess of magnesium oxid to a solution of gold trichlorid, and removing the excess of the former by means of dilute nitric acid. The hydroxid is insoluble, and is left behind as a yellow powder. The hydroxid ($Au(OH)_3$) loses three molecules of water when heated to 100°, leaving gold trioxid (Au_2O_3). This compound is easily decomposed at temperatures of about 250°, and also by the action of sunlight. The oxid and the hydroxid both dissolve in the fixed alkali hydroxids, forming salt-like compounds, —

$$KAuO_2, \quad O=Au-O-K.$$

Aurous oxid (Au_2O) has also been prepared. Ammonium hydroxid forms a reddish yellow precipitate in a solution of gold trichlorid. This is a very explosive compound called fulminating gold.

But one gold sulfid is known (Au_2S_3) corresponding with the trioxid. It is produced by passing hydrogen sulfid into a solution of auric chlorid. It is a yellow solid, insoluble in hydrochloric acid, but it is soluble in ammonium sulfid. These facts place gold among the metals whose sulfids are precipitated from acid solution (HCl), and along with arsenic, antimony, and tin, owing to the solubility of its sulfid in ammonium sulfid.

PLATINUM.

Occurrence and Distribution. — Platinum is found in but few localities, and when found occurs in small quantities. It is found in California, in the Ural Mountains, in Brazil, and in Australia. It occurs native, but is usually alloyed with a number of other elements much resembling platinum in their

properties. It is found principally in alluvial deposits and often along with gold, and occasionally it occurs combined with arsenic as an arsenid ($PtAs_2$).

Preparation. — The problem to be solved in preparing platinum is to free it from its alloyed metals. The mining of the ore is very similar to that of gold. The purified ore contains from 20 to 30 per cent of the metals alloyed with platinum. These metals are gold (sometimes), osmium, iridium, rhodium, ruthenium, and palladium. (The latter elements are briefly described later on under CLASSIFICATION, but the reader is referred to larger works like Roscoe and Schorlemmer's treatise for detailed descriptions.)

After the platinum ore has been freed as much as is possible from mechanical impurities, it is treated in one of the two following ways to purify it.

(*a*) It is treated with dilute aqua regia, which dissolves out the gold, if present. This is washed away, and concentrated aqua regia is added, which dissolves all of the platinum and most of the other metals, except osmium and a portion of the iridium, in the form of the chlorids. The solution is concentrated and treated with ammonium chlorid, which forms insoluble compounds with platinum and iridium of the form $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$. This precipitate is dried and ignited, when the compounds are decomposed, leaving platinum and (a little) iridium in a finely divided condition (platinum sponge). This is afterwards fused in an oxy-hydrogen furnace.

(*b*) The oxy-hydrogen furnace is also used to separate the metal from its ore. The furnace is made of lime. A cavity is made in a thick block of lime, which serves as the base of the furnace. The cover is made of a thinner block, which has a similar cavity cut in it, and is pierced through the center for the admission of the oxy-hydrogen jet. A small opening is left at one side. The purified ore is placed in the furnace and heated to the temperature of the oxy-hydrogen flame. At this

temperature the ore fuses. It is kept at this temperature for some time, during which time some of the impurities unite with the calcium oxid, and osmium is vaporized and escapes. There is left a little iridium (possibly some rhodium) alloyed with the platinum. For most purposes, this platinum is sufficiently pure.

Properties of Platinum. — Platinum somewhat resembles silver in appearance, but is of a grayish white color instead of a silver white. It is one of the heaviest metals, osmium and iridium (sp. gr. 22.42) being the only ones that are heavier. Its specific gravity is 21.5. It is next to gold and silver in its ductility and malleability. One of its most useful properties is its infusibility in any but the highest producible temperatures. The metal is harder than copper and softer than iron. The finely divided platinum (sponge) is dull gray in color. Platinum absorbs gases, especially hydrogen, to a remarkable extent. The amount absorbed depends on the fineness of the division of the metal.

Platinum black (made by precipitating the metal from its solution by other metals like zinc) can absorb 800 volumes of oxygen for every volume of platinum. This oxygen is far more active chemically under these conditions than is ordinary oxygen, and it is used to oxidize other substances. For example, sulfur trioxid is made by passing air and sulfur dioxid over platinum black. (Platinum sponge will absorb about 200 volumes of oxygen.) Platinum forms alloys with most of the metals.

Chemical Properties. — Platinum belongs to the class of inert metals. It is not attacked by the air at any temperatures. It is not dissolved by any of the ordinary acids, such as sulfuric, hydrochloric, nitric, hydrofluoric, and hydriodic acids. It is attacked by nascent chlorin or bromin. It is therefore dissolved in aqua regia, forming the platinum chlorid. It is a notable fact that platinum when alloyed with silver is oxidized

and dissolved by nitric acid. At red heat, alkalis act upon platinum, probably owing to the formation of alkali platinates at this high temperature. Several of the non-metallic elements act on the metal at high temperatures, such as arsenic, phosphorus, sulfur, and silicon. Organic matter containing phosphorus should not, therefore, be heated in platinum vessels. Compounds containing the elements mentioned in easily reducible form (nor the elements themselves) should not be heated in platinum vessels.

Name and History. — Platinum was discovered in the early part of the eighteenth century, and was found in South America. Many of its properties were discovered during the latter half of this century, but it was not until its discovery in the Ural Mountains, about 1830, that it came into use. In fact, it was not until the studies of Deville and Debray (1850–1860) that methods for its production were sufficiently developed to permit its extended use. The name *platinum* is derived from the Spanish word, *plata*, for silver. It is the diminutive of this word (*platina*) and therefore signifies *small silver*.

Atomic Mass and Valence. — Platinum, like gold, does not form many compounds that are stable, and all of them are decomposed at raised temperatures. The determination of its atomic mass, therefore, depends on analytical methods and the method of specific heat. By the former method the atomic mass is 194.3. The specific gravity of the element is .032, which gives for its atomic mass a number very close to this one. Analysis of the compounds of chlorin and platinum shows that 194.3 parts of platinum correspond to 141.48 parts of chlorin; but 141.48 parts of chlorin is four atoms of chlorin. A chlorid containing one-half as much chlorin is known. Platinum is, therefore, bivalent and quadrivalent.

Uses. — The chemical inactivity and the infusibility of platinum make it a valuable substance for use in various manufacturing and technical operations. Its use in making certain

forms of apparatus has done much to advance both theoretical and practical chemistry. It is employed in the form of wire and foil and to make vessels and tubes. Sulfuric acid is dehydrated in stills made of platinum, some of them weighing from 40 to 50 kg., and costing several thousand dollars. Platinum is attacked at red heat by the fixed alkali hydroxids, many sulfids, and the cyanids. It readily alloys or combines with sulfur, arsenic, antimony, tin, lead, gold, silver, and bismuth. An alloy of platinum with iridium, in the proportion of 90 of platinum to 10 of the iridium, possesses many valuable properties. It is very hard, and very resistant to the action of most chemical agents. Many compounds containing these elements are reduced by platinum at high temperatures. Carbon unites with it at high temperatures. This fact is seen when the bright surface of a platinum crucible is heated for some time in a sooty flame. It becomes dull and loses in mass.

Compounds of Platinum.

The two oxids and the corresponding hydroxids of platinum are known. The oxids are produced from the hydroxids by driving off water at a comparatively low temperature. The hydroxids are formed by adding a soluble hydroxid to the solutions of the chlorid. When the precipitates are dried at 100°, they yield the hydroxids, platinous and platinic $Pt(OH)_2$ and $Pt(OH)_4$. Platinous hydroxid, when treated with dilute acids in the cold, forms unstable salts.

Platinic hydroxid is an acid, forming a class of salts having the form R_2PtO_3 corresponding to an acid H_2PtO_3. Platinic hydroxid dissolves in potassium hydroxid, forming the compound K_2PtO_3. Many other bases form salts with this acid, which are called platinates.

The halogen salts of platinum are its most stable compounds. Platinic chlorid is the source of most of the other compounds

of the metal, and is prepared, as previously described, by the solution of platinum in aqua regia. It crystallizes from water solution with usually 5 to 10 molecules of water, according to conditions. This chlorid unites with molecules of hydrogen chlorid, the compounds of which crystallize out with water. Its most common compound is $2\,HCl.PtCl_4$ or H_2PtCl_6. (Compare with auric chlorid.) This compound is an acid, and forms salts called chlor-platinates. The most noticeable of these compounds are those of potassium and ammonium, K_2PtCl_6, and $(NH_4)_2PtCl_6$. These salts are insoluble, while all the other salts of these metals are soluble. These are golden yellow precipitates, almost absolutely insoluble in alcohol. The corresponding sodium salt is soluble in water and in alcohol. Use is made of these facts in separating sodium from potassium compounds. The salts of these metals are changed to the chlorids, and then they are treated with platinic chlorid ($PtCl_4$). Alcohol then is added to the mixture, and the potassium and platinum chlorid is filtered out. Platinum also forms double cyanids similar to those of gold. They have the form, as shown by the potassium salt, $2\,K_2CN.Pt(CN)_2$ or $K_2Pt(CN)_4$.

Platinum forms two sulfids, PtS and PtS_2, when the platinous and platinic chlorids are treated with hydrogen sulfid. These sulfids are soluble in yellow ammonium sulfid. They are thus included with the sulfids of arsenic, antimony, and tin, since, when a mixture of the sulfids of the metals which are insoluble in hydrochloric acid is treated with yellow ammonium sulfid, the platinum sulfids are dissolved or separated with the sulfids of these elements. Platinum can be recognized by dissolving this sulfid in aqua regia, freeing the solution of the excess of acid, and treating with a concentrated solution of potassium carbonate or of potassium chlorid.

The elements mentioned as occurring with platinum — *i.e. ruthenium*, *rhodium*, *iridium*, *palladium*, and *osmium* — resemble it in many of their properties. Their atomic masses are in

the order named: 103.5, 104.1, 106.2, 191.1, 192.5. They are all found free in nature in small quantities associated together with platinum. They all form compounds with the halogens, and generally the two classes of compounds represented by the formulæ RCl_2 and RCl_4. The oxids and hydroxids are either feebly basic or feebly acid. Some of the hydroxids act in both ways, depending on the conditions imposed; *e.g.* platinum hydroxid ($Pt(OH)_4$) dissolves in dilute acids and in dilute alkalis. Some of the oxids are neither acid nor basic. The compounds are readily decomposed, and the metal is set free. This fact is applied when a solution of osmic oxid (called osmic acid) (OsO_4) is used to stain microscopical preparations of animal tissues. The tissue is stained black by the reduced metal.

Palladium resembles platinum in many of its physical properties. Among these properties is the property of absorbing gases. This is often really regarded as a chemical property. The combination with hydrogen is probably of the nature of an alloy. Palladium foil absorbs 370 times its own volume at ordinary temperatures, and 650 times this volume at 100°. When the metal is finely divided like platinum black, it absorbs 900 volumes of hydrogen. The new combination has a lower specific gravity than the pure metal, and is represented by the formula Pd_2H. This substance gives up its hydrogen completely at red heat. The powdered metal is used as an absorber of hydrogen in gas analysis. The palladium hydrid gives up its hydrogen to oxygen at ordinary temperatures; it therefore is a powerful reducing agent. The reader is referred to larger works for other facts in reference to these elements.

Experimental Study, No. 17. — Use solutions containing soluble salts of the elements of mercury (Hg), lead, arsenic, antimony, tin, bismuth, copper, cadmium (platinum and gold). Several combinations may be prepared by the instructor. For example, solutions containing lead and arsenic, arsenic, anti-

mony, and bismuth, etc. These elements are to be separated and recognized while in combination, by the facts in reference to the solubility in water, and other reagents that have been established in the preceding studies of these elements and their compounds. Dry salts should be tested on charcoal for the purpose of recognizing these elements. These elements constitute what is called Group II.

Suppose that a solution containing the compounds of all of these elements is used, what is the effect of passing hydrogen sulfid into it? What is the effect of having the solution acidified by hydrogen chlorid? (Slightly acid and very acid?) What is the result if dilute nitric acid is used? What is the effect of treating this original mixture with a soluble sulfate or with sulfuric acid? Write a scheme of separation on this basis. What is the result when this solution is treated with a fixed alkali hydroxid? With ammonium hydroxid?

What happens (*a*) when the sulfids of these elements are acted on by ammonium sulfid (yellow)? (*b*) When they are treated with nitric acid? Suppose arsenic, antimony, and tin are removed, and the remaining sulfids are treated with nitric acid? Into what sub-groups will ammonium sulfid and nitric acid divide these elements? How can these sub-groups be further separated? In what combinations are these elements after treating with these two reagents? Suppose that lead, bismuth, copper, and cadmium are in solution as the nitrates, what is the result of adding sulfuric acid to it? If the lead is absent in such a mixture, and ammonium hydroxid is added in excess, what occurs? If KCN is added to this solution (after filtering, if necessary), what is the result? What is left in solution? What is the effect of passing H_2S into this solution? If a compound of each element is separated from all the others, how can each be recognized?

If arsenic, antimony and tin are precipitated as sulfids together, they may be separated by dissolving them in hydro-

chloric acid in which is placed a few small pieces of potassium chlorate. The whole is heated, and more of the chlorate is added if necessary to dissolve the sulfids. (Sulphur is set free, and should be distinguished from the metallic sulfids. It floats on the surface of the liquid. No more chlorate should be added than is necessary to dissolve the sulfids.) The solution is evaporated until all of the free chlorin is driven off. It is then transferred to the hydrogen generator while the hydrogen is escaping. Pass the gas into a solution of silver nitrate. Where are the arsenic, antimony, and tin? See Part I. for the recognition of arsenic and antimony. The tin is deposited on the zinc, from which it can be separated and recognized. How?

What can be learned from the color of the precipitate that is made in the original solution by hydrogen sulfid?

In general, each precipitate that is to be separated and recognized must be well washed before this work can be done. The object of the washing is evident when any given case is considered. Examine the precipitate formed in the first group as it lies on the filter. It is readily seen that it holds free hydrogen chlorid and portions of the salts of any other metals that may be present in the original solution. Let one of these salts be copper sulfate. If it is not washed away when ammonium hydroxid is added to dissolve out the silver chlorid, the solution becomes blue and thus obscures the other test. In washing, the funnel is filled with pure water, and it is allowed to run through before more water is added. Explain why. Suppose the impurity which is retained in or by the precipitate is held in solution by 15 cc. of water, and that it is equal to 1 g. of a solid. 50 cc. of pure water are added. How much is there left of the soluble solid when the water has run through, leaving the 15 cc. of water held by the precipitate?

Experimental Study, No. 18.—Solutions containing members of both Groups I. and II. should be studied for the purpose of the separation of one group from another, and also for further

study within the groups. The reactions occurring in all the changes in this separation referred to, in this and the last study, should be written out and grouped under the head of group reactions. The reactions occurring that have not been studied before are those of potassium chlorate described in the method of separating arsenic, antimony, and tin. They are —

(a) $As_2S_3 + 10\,Cl + 8\,H_2O = 2\,H_3AsO_4 + 10\,HCl + 3\,S$;
(b) $Sb_2S_5 + 6\,Cl = 2\,SbCl_3 + 5\,S$;
(c) $SnS_2 + 4\,Cl = SnCl_4 + 2\,S$;
(d) $2\,KClO_3 + 4\,HCl = 2\,KCl + Cl_2 + (Cl_2O_4 = Cl_2 + 2\,O_2) + 2\,H_2O$.

The chlorin for these reactions is set free by the action of hydrogen chlorid on the potassium chlorate. (See (d).)

IRON.

Occurrence and Distribution. — Iron is one of the most widely distributed and most abundant of the elements. As the result of the analysis of many samples of the material of the earth's crust, iron is placed fourth in reference to the quantity found in that portion of the earth of which we know. When so placed, oxygen stands first, or constitutes 480 parts in 1000 parts of the earth's crust. Silicon is 290, aluminium 80, and iron 60. Iron not only is widely distributed in the earth's crust, but it is also found in space outside of the earth. This is evidenced by the great amount of it that falls upon the earth from time to time. This iron is quite generally uncombined except where it has come in contact with our atmosphere. These masses, called meteors, vary in size from very fine dust particles to masses having a mass of many tons. A mass of meteoric iron has been found in Peru that weighs over fifteen tons. This meteoric iron is not pure, but always contains nickel, and often small amounts of other elements such as cobalt, manganese,

carbon, etc. Iron is essential to plant and animal life, and is taken up by the former from the soil.

The principal localities in which the ore is found, in the United States, are in Pennsylvania, Wisconsin, Minnesota, Michigan, Washington, and Alabama; in Europe, Sweden, Norway, and England furnish immense quantities of valuable ore.

Iron has great affinity for oxygen and sulfur, and consequently the great mass of the iron of the earth is combined with these elements. The bisulfid of iron (FeS_2), called iron pyrites, is the most widely distributed of the compounds of iron, but it does not serve as an ore, because of the difficulty of removing all the sulfur from it and the injurious effect that this small amount of sulfur has on the properties of the iron. It occurs in large masses and in a very pure condition. It is crystalline in structure and has a metallic appearance.

The next most abundant ores of iron are the oxids and hydroxids; and they are the chief source of the metal. The carbonate is also quite abundant in certain localities such as England, and is a source of much of the iron of commerce. This ore is known as siderite. The composition of these ores will be taken up under COMPOUNDS. Both the oxid and the carbonate occur in both amorphous and crystalline masses.

Preparation.— As has been said, the ores of iron are the oxids, hydroxids, and carbonates. The carbonates and the hydroxids are, however, easily decomposed into the oxids, carbon dioxid, and water. The problem is, consequently, how shall the oxygen be separated from the iron? There is also the other problem, that has been referred to in the study of other metals, and that is the one of separating the iron from accompanying impurities, many of which seriously injure the iron for its common uses. These impurities are those of the wall-rock, clay, silica, sulfids, compounds containing phosphorus, and limestone. The action of such substances as hydrogen, carbon monoxid, and carbon to remove oxygen from oxids has already

been studied. All of these substances will remove the oxygen from the oxids of iron. It will be noticed that carbon has been most commonly used for this purpose. However, the metals thus far studied can be easily fused, and the molten metal being heavier than the non-metallic impurities sinks through the mass and can thus be separated.

Iron is a very infusible substance, and does not, when pure, melt at the temperatures produced by the oxidizing of carbon or fuel, and hence the method that has been applied to separate lead, for example, from oxygen, cannot be used here. The iron of the oxid, when it is reduced, is in the form of a fine powder. In spite of the fact that pure iron does not fuse readily, it does become pasty, and the fine particles adhere or weld together to a certain extent at high temperatures.

Another property of iron, however, is brought into use in its reduction. Iron has the property at high temperatures of uniting with a small amount of carbon (up to 6 per cent) and, due to this combination, becomes fusible at temperatures that can be produced by the oxidizing of carbon. To get rid of the other impurities, a substance called a flux (*fluo*, to flow) is added to the mass of ore and carbon, which unites with these impurities to form a fusible mass. This substance is always lighter than the iron, and through which the latter passes to the lowest part of the including vessel.

The essentials of the apparatus in which iron is prepared are a closed vessel made of material that does not fuse or disintegrate at high temperatures, and at the same time does not conduct away heat, or only a minimum amount. In order that the process shall be commercially useful and profitable, it must be arranged so as to be used continuously. The description in detail of this apparatus, which is called a blast or smelting furnace, belongs to works on technology. Suffice it to say that the furnace is built in the form of a tower or chimney, and varies in height from about 30 to 90 feet. The central

cavity is double cone-shaped (the cones being joined at their bases), and varies in diameter, at the largest part, from a few feet to 17 feet. The lower cone terminates in a cylindrical part called the hearth. There are also means for drawing off the molten iron and slag that accumulates in the hearth, for admitting air under pressure, for charging the furnace, and for carrying off the gases which result from the action that goes on in the furnace. The latter two are at the top of the furnace. When once such a furnace is charged and heated up, the action is kept up during its life, which is from two to twenty years.

The charge of the furnace consists of fuel (coke or anthracite coal), ore, and fluxing material, usually about 150 kg. of coal to 200 lbs. of ore, depending on the ore and to some extent on the fuel. When the combustion is once started, air is blown in at the hearth, and rapid combustion is kept up. The temperature gradually decreases as the top is approached. It ranges from about 2600° at the place of greatest chemical activity to about 400° near the top. The temperature is greatest, therefore, near where the blast of air enters the furnace.

Let us examine what the changes (mainly physical) are that occur in the charge as the combustion progresses, supposing the furnace has been "in blast" for some time, and when it is full of the materials which are arranged in layers of fuel, ore, and flux, the three layers alternating from the bottom upwards. As the fuel is consumed and the other material aggregates together, the same materials are added at the top. (The ore is usually prepared by roasting it, in order to oxidize some of the impurities, to drive off the moisture, to decompose the hydroxids and carbonates, and to oxidize any ferrous iron to the ferric form, in which condition it is more readily reduced.) Beginning at the top and passing downward, it is noticed that the temperature rises, and between the limits of 400° to 600° the materials are being heated (and if the ore has not been

previously dried, etc., by roasting, the changes just described under this process occur). The flux is dried, and the lime of the latter is decomposed. (See under CALCIUM CARBONATE.) Between 600° and 1200° the iron is reduced and welds together into a more or less adherent mass. From 1000° to 1600° the iron unites with the carbon; and as the mass moves downward, the iron fuses, the fusion becoming complete between 1600° and 2000°. The melted mass now passes by reason of gravity to the base of the hearth, where it accumulates, and from whence it is drawn off from time to time and cast into bars called cast or pig iron.

The chemical changes are best studied by starting at the hearth where the air enters. The complete account of these changes cannot be given, since some of the questions connected with them are not yet settled. Yet in general the changes are well understood. Where the air enters the furnace, there must be the greatest and most rapid combustion, and hence this is the hottest part of the furnace. It is generally stated that here carbon dioxid is produced, and that the gas, as it passes up through the hot material, comes in contact with the carbon and is decomposed into carbon monoxid; one molecule of the dioxid becoming two molecules of the monoxid. In ordinary combustion where there is a large supply of oxygen and the temperature is not too high, carbon dioxid is the usual product of the oxidation of carbon. It is, however, claimed that even here there are two stages in the oxidation, — namely, the formation of carbon monoxid, — and from this oxid and more oxygen the higher oxid is produced. But in this case the temperature at this point of greatest combustion is not far from 2500° to 2600°, and at these temperatures carbon dioxid does not exist; *i.e.* it is dissociated at these temperatures. It therefore appears most probable that carbon monoxid (CO) is principally formed at the hottest parts of the furnace. Other gases like methane (CH_4) and cyanogen (CN_2) are also

formed at different points in the furnace. As the hot gases move upwards, it is probable that some of the carbon monoxid unites with the oxygen and forms carbon dioxid; but before reaching temperatures sufficiently low for the latter action, most of the oxygen has already combined with carbon. The gaseous substances that are moving up through the furnace are then nitrogen, carbon dioxid, carbon monoxid, methane, and cyanogen; the two latter gases are found in relatively small quantities. The gases, — *i.e.* CO, CH_4, $(CN)_2$, and a small amount of free hydrogen, probably from water vapor in the air, — as they move upwards, and when they reach the portion of the furnace where the temperature is between 800° to 600°, unite with the oxygen of the ferric oxid, setting the iron free in the form of minute particles, which weld loosely together and receive carbon and silicon a little later as they move downward and become fused.

The various gaseous products become reduced in temperature through the heating of the new material, and the work of dissociation of the lime (calcium carbonate), the hydroxids, etc., and the decline in temperature from the bottom upwards, is more rapid than it is in an ordinary chimney. The reactions that occur are represented thus: —

$$Fe_2O_3 + CO = CO_2 + 2\,FeO;$$
$$FeO + CO = CO_2 + Fe;$$
$$3\,CH_4 + 4\,Fe_2O_3 = 8\,Fe + 6\,H_2O + 3\,CO_2 \text{ (or CO)};$$
$$3(CN)_2 + 4\,Fe_2O_3 = 8\,Fe + 6\,CO_2 + 3\,N_2;$$
$$Fe_2O_3 + 3\,H_2 = 2\,Fe + 3\,H_2O.$$

Beginning with the iron after it has taken up carbon and silicon in its downward movement, it will be noticed that it is approaching the part of the furnace where there is free oxygen, and that it must pass through the region into which the supply of oxygen comes. To prevent the iron (as much as possible)

from coming in contact with the oxygen, and thus becoming partly oxidized, the fluxing material comes into use. The materials of the flux which have been added to the charge, or which were naturally with the ore, are each of itself infusible; but when there is the proper proportions of its parts, they unite at the temperature of the furnace, and form a fusible mass called the slag. The amount of limestone added must be just sufficient to unite with all the silica (SiO_2); since if it is not in sufficient quantity, the latter unites with some of the iron to form iron silicate ($FeSiO_3$). If too much is added, it being infusible, it clogs the furnace and prevents the downward movement of the charge. This runs down with the iron, envelops it, and protects it from the oxygen of the "combustion region."

Some of these changes in the fluxing material are represented thus: —

$$CaCO_3 = CaO + CO_2;$$

$$CaO + SiO_2 = CaSiO_3;$$

$$FeO + SiO_2 = FeSiO_3.$$

Unfortunately, as the iron approaches the hearth, it takes up small amounts of sulfur from the fuel and phosphorus from the ore; the latter element, having been reduced by the carbon from its compounds in the fuel, unites with the iron. These elements impart properties to the product that render it unfit for many uses.

Formerly the gaseous products were allowed to oxidize at the mouth of the furnace. In most cases now, the furnace is closed at the throat by a conically shaped apparatus which can be readily opened when it is necessary to add a new charge. Pipes open into the furnace just below the throat, and the gases are conducted away and oxidized under boilers which furnish power to "run" the air-blast. The heat of this combustion is

also used to heat the air-blast, so that the air enters the furnace at a temperature of about 700° (from 400° to 700°).

An average modern furnace uses about 300,000 l. of air per minute.

The iron produced by the methods just described in outline is called cast, or pig iron, and possesses properties quite different from the pure metal. A study of cast iron will be taken under the topics, KINDS OF IRON.

Experimental Study, No. 19. — (*a*) Examine pieces of iron for physical properties such as structure, hardness, and color.

(*b*) Determine the specific gravity of iron by first weighing a piece of it, and then dropping it into a graduated cylinder partly filled with water, *i.e.* with sufficient to cover the iron. Note the apparent increase in the volume of the water. To what is it due? (At 16° a cubic centimeter of water weighs .999002 g.) What is the volume of iron?

(*c*) Heat about 5 g. of tartrate of iron in a narrow test-tube until decomposition is complete. Cool the tube, and while quite warm stop the tube tightly, and cool to ordinary temperatures. Remove some of the residue, and examine it with a magnet. Explain the result. Allow the residue to fall through the air. Note and explain the result.

(*d*) Weigh a porcelain crucible, and place it in 3 to 5 g. of powdered iron (the exact weight must be known). Heat this in the lamp, constantly stirring it with an iron wire until the action is complete. Cool for some time, and weigh again. To what is the increased mass due? Determine the proportion of iron, the oxygen being taken at 16.

(*e*) Transfer the oxid of iron produced in (*d*) (or a portion of it) to a hard glass tube, heat it to red heat, and while at this temperature pass through it dry hydrogen. Cause the products to pass through a cooled tube. (A glass tube bent to a wide-open V, the bend of which is placed in cold water, can be used as a cooler). Pass the gas until the red color disappears. Cool and examine the residue. What is the product?

(*f*) Weigh out about .5 g. of pure iron piano wire; next invert a graduated tube filled with dilute sulfuric acid (1 to 5) in a sufficiently large vessel, like a six-inch evaporating-dish, containing enough of the dilute acid to cover the mouth of the tube. Quickly place the weighed iron under the mouth of the tube. Leave it here until the action is complete. When the tube has cooled to the temperature of the room, measure the volume under atmospheric pressure, and calculate the volume of hydrogen under standard conditions. What is its mass? Consider the amount of hydrogen as unity, what is the iron? Double the number. To 50 cc. of the solution used in dissolving the iron add more iron, such as nails, and warm as long as any of it dissolves, adding more iron if necessary. Filter the solution, and set aside for further study. Examine the black residue. Dry some of it, and placing some of it on a platinum wire, heat it in lamp flame. What is it?

(*g*) Study the action of hydrochloric and nitric acids on a few grammes of iron. What are the gaseous products in each case? Write the reactions. Save the solutions for further study. Make two solutions in nitric acid, one in cold dilute acid, and the other in hot fairly concentrated acid. Always use an excess of iron. Pass chlorin gas into a portion of the solution of iron in hydrochloric acid. Note change of color. Boil to drive off the free chlorin. Save all of the solutions for Study 21.

(*h*) Place a few grammes of powdered iron in a test-tube, and add about twice as much iodin and a little water that has been well boiled. Grind them together until most of the iodin disappears. Filter out, and save the solutions for further study.

(*i*) Heat sulfur and iron together. Cool, and treat the product with dilute sulfuric acid. What is the product? Write the reactions.

(*j*) Pass through the tube containing the reduced iron of (*e*) a stream of dry chlorin gas. The tube is strongly heated during the time the chlorin passes through it. What are the

crystals that are formed on the sides of the cooler parts of the tube? Use a tube for cooling similar to the one used in (*e*). Dissolve some of the product in water, and test for combined chlorin. Save for next study.

Physical Properties. — Pure iron is a silver-white metal of great ductility, and a tenacity greater than that of any other metal, cobalt and nickel being excepted. (The pure iron is best obtained by the action of a weak current of electricity upon a ferrous salt. Or, the pure iron may be prepared from the pure oxid by reducing it in hydrogen and then fusing the iron out of contact with the air.) Such iron is quite soft, and can be rolled into very thin sheets. Its fusion point is very high; in fact, it does not become perfectly liquid at any temperature that is readily produced. It, however, softens, and becomes so plastic at high temperatures that it can be rolled, welded, and worked into almost any form. It has a specific gravity of 7.84. The pure iron is not magnetic, but is attracted to the magnet, and becomes magnetic while in contact with it. When the contact is broken, it no longer possesses this property. The purer the iron, the more quickly does it lose its magnetic properties.

Chemical Properties. — Chemically speaking, iron is an active element, and especially so at high temperatures. It possesses the property common to many substances, — that of being chemically inactive when thoroughly dry or free from moisture. Dry air does not attack or oxidize iron; but when moisture is present, it oxidizes rapidly, forming what is called rust. Other substances that may be present in the air aid in the rusting of iron. These are carbon dioxid, and small amounts of acids, the halogens, etc. It is said that water entirely free from dissolved oxygen has no action on the metal. The rust that is ordinarily formed on iron is a basic hydroxid.

The acids (hydrochloric, sulfuric, and nitric acids) all act readily on iron, forming corresponding salts. The first two

acids set hydrogen free, while the nitric produces the usual products.

When iron is placed in steam heated to a temperature of 650°, the steam is decomposed, hydrogen is set free, and the triferric tetroxid (Fe_3O_4) is produced on the surface of the metal. This forms an adherent coat which protects the iron from oxidizing or rusting. This fact is made use of to prevent iron from rusting in the so-called Barff process. The halogens and sulfur readily unite with iron. The halogens form two classes of compounds. One class is illustrated by the compound formed with iron when it is acted upon by hydrochloric acid, or by dry hydrogen chlorid, and the second class by the compound formed when this compound is treated with free chlorin, or when iron is treated with free chlorin at high temperatures.

Name and History. — This most useful metal has been known from the earliest times, even before the time of authentic history. It is said that iron has been employed in Egypt for the purpose of making tools for more than 5000 years. Just when the process of separating it from its natural combinations was discovered is not known, but it is of very early origin. The name *iron* is of ancient origin, and probably signified a metal. The symbol Fe is derived from the Latin word for iron, *ferrum*.

Atomic Mass and Valence. — The atomic mass of iron has been determined in many ways. As early as 1811, Berzelius made this determination; and although the number that he obtained was too small, and great accuracy could not be expected, it was among the first of such determinations. Later his attention was called to his error by other workers, and he started new determinations, and in the year 1850 he fixed the number at 56. The principles of the method used have been illustrated in the last study. Pure iron is weighed and oxidized, and again weighed. These results, after the

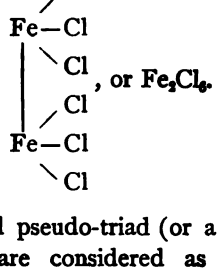
work has been repeated several times, show the amount of iron that unites with a given quantity of oxygen. On the basis that the atomic mass of oxygen is 16, the corresponding amount of iron is calculated. The oxid is now decomposed by hydrogen, and the amount of oxygen removed is determined. According to the atomic theory of matter, the proportion in which these two elements have united is either the atomic proportions, or they are multiples of these numbers.

Many facts are brought together, however, and from a study of these facts the number is selected. For example, in the last study it was discovered that one part of hydrogen is equivalent to 27.94 parts of iron; *i.e.* 1 g. of hydrogen is set free by 27.94 g. of iron. On the other hand, iron forms but one (-ous) sulfate, which means, in connection with all the facts known, that it always sets two atoms of hydrogen free at one time from all acids. This amount of iron, it is readily seen, is represented by 55.88.

Again, iron forms a compound with chlorin that is capable of being volatilized. The vapor density of this compound is nearly 81. Quantitative analysis shows that this molecule contains 55.88 parts of iron and 106.11 parts of chlorin. From these facts and similar ones, the atomic mass of iron is fixed at 55.88 (56 when oxygen is 16).

It has been stated that 56 parts of iron (or the atom) replace. two atoms of hydrogen in acids, thus indicating that iron is in these cases bivalent. In the compound of iron with chlorin, it is seen that the atom of iron is combined with three atoms of chlorin, and therefore that iron is also trivalent. These two classes of compounds (or salts) are recognized and are distinguished as ferrous and ferric compounds. The formula for this ferric chlorid is often doubled, since iron is often regarded as quadrivalent. The explanation of its apparent trivalence is made by saying that a unit of valence of each of two atoms of iron is used to hold the atoms together, thus leaving six unsat-

isfied units of valence for each two atoms. The compound with chlorin is represented thus:—



, or Fe_2Cl_6.

Iron is then called pseudo-triad (or a true tetrad), and all ferric compounds are considered as having this atomic group, Fe^{VI}_2.

Kinds of Iron, and its Uses.—The iron that is employed for ordinary purposes is not the pure metal, but contains impurities that are due to the composition of the ore, fuel, and flux, and the method of manufacture. Some of these impurities give to the iron valuable properties (*e.g.* carbon), and some of them render it unfit for a great variety of uses.

Commercial irons are arranged in three classes; namely, cast or pig iron, wrought iron, and steel. There are several varieties of each class.

Experimental Study, No. 20.—Material: Samples of varieties of pig and wrought iron in the form of cuttings.

(*a*) Treat each of the samples with hydrochloric acid, and note the residue, and the gases that escape, the amount of carbon set free, with the different samples. Dry some of the residue from the black or mottled cast iron and attempt to ignite it.

(*b*) Heat a piece of cast iron to a bright red and cool it suddenly in cold water. Weigh out 10 g. and dissolve it in acid. Filter out the residue, dry and weigh it.

(*c*) Heat the same kind of iron (as was used in (*b*)) to bright red temperature and let it cool slowly. Examine the

fracture of (*b*) and (*c*). Weigh out 10 g. of this iron and treat it as in (*b*). Compare the weights of the residues. It is well also to collect the gases produced in each case and compare the amount of one with that of the other.

(*a*) **Cast Iron.** — Cast iron is the source of the other two kinds of iron. They are made from it by removing or changing the amounts of the impurities contained in the former.

Cast iron contains from 2 to 6 per cent of carbon, from .08 to 4.77 per cent of silicon; sulfur (in many samples), none to 1.06 per cent; phosphorus, a trace to 1.87 per cent; and manganese, from .116 to 6.08 per cent. There are often small amounts of other impurities which slightly modify the properties of the cast iron. The impurities just given have quite different effects on the properties of the iron. The amount of these impurities just given represents the extremes for each substance. Without entering into details of the effect of each of these constituents, it may be well to briefly notice their effect in order that the reason for their removal or change may be more evident.

The carbon produces effects depending on the manner of its combination in the iron and on how much there is present. In general, it makes the iron hard and brittle and, in connection with other impurities, restricts its use to structural purposes for which the iron is cast into the required form. Such iron cannot be forged, welded, or rolled into plates. It can be melted, however, and since it possesses the property of expansion at the temperature of solidification, it can be cast into any desired form. Cast iron is strong in the sense that it will resist a crushing force, and consequently its structural use is generally for supports and similar purposes. Cast iron is dark gray to white or mottled in color, and granular or crystalline in structure. It was noticed in Study No. 20 that when the dark iron was dissolved in acid, there was a black residue of carbon. This is found to be graphite. It was also noticed that when the gray

iron was heated and suddenly cooled, that the color was changed, and that less of the graphite was set free when it was dissolved in acids. It has been discovered that the carbon exists in the iron as graphite, and also in combination with the iron. The combined carbon unites with the hydrogen of the acid to form hydrogen compounds of carbon. Some of these compounds have a disagreeable odor which characterizes the gases that escape when iron is dissolved in acids.

The amount of the combined carbon in cast iron depends to a great extent on the temperature of the iron and the rapidity of the cooling at the time that it leaves the blast furnace, as well as on the ore and conditions of the furnace, which determine the amount of carbon taken, etc. When cast iron is fused and suddenly cooled, the carbon is mostly left in the combined condition. If it is slowly cooled, most of it is left in the graphitic condition. The varieties of cast iron depend upon the facts just given. If the iron is cooled suddenly as it comes from the blast furnace, the iron is white and crystalline, and is called white iron. The presence of manganese in the ore causes the iron to take up more carbon, and such iron is usually white. It is called spiegeleisen; and when there is much manganese, it is called ferro-manganese. It may contain as high as 6 per cent of carbon. When the iron cools slowly, the carbon is not retained as combined carbon, but is left as graphite. The black graphite disseminated through the white iron gives the mass a gray appearance. Such samples are called gray cast iron. This iron fuses at lower temperatures than does the white iron, and is used for making castings. Another variety of iron has the graphite irregularly arranged in the iron, giving it a mottled appearance, and is called mottled iron. These three main varieties of cast iron grade into each other, practically giving a great many varieties.

(*b*) **Wrought Iron.** — Of the 6 to 10 per cent of impurities found in cast iron, from less than one-half per cent to nearly

3 per cent are sulfur and phosphorus. These elements injuriously affect the working properties of the iron even if the carbon (and silicon) did not render it too brittle for forging, etc. The sulfur makes the cast iron brittle when hot, called "red-short"; and phosphorus produces a like effect when the iron is cold, called "cold-short," and, therefore, is more injurious to the iron for most uses than the sulfur. More than a few hundredths of 1 per cent of either of these elements is injurious to the metal for its usual purposes. The best wrought iron is entirely free from these elements. It is very infusible, requiring at least a temperature of about 2100° for complete fusion. What is sought then in making wrought iron is to remove as nearly as possible all these impurities, although one-half of 1 per cent or less of carbon does not affect injuriously to any great extent its working properties. Such iron can be welded and hammered, and does not harden when suddenly cooled. The process of manufacture makes it very tough and often fibrous. The excess of carbon, silicon, sulfur, and phosphorus are removed by oxidation.

This oxidation is carried on by several methods. The puddling process was brought into use in 1784 by an Englishman named Cort. This method as now employed consists in melting the cast iron in a reverberatory furnace, the lining of which is made of quite pure ferric oxid or of pure hematite ore. Air is made to pass over the surface of the molten iron, and it is stirred in order to bring the unchanged iron to the surface, and also to bring it in contact with the oxid lining. The oxygen of the air and that from the oxid of iron gradually oxidize the impurities. The silicon becomes silicon dioxid (SiO_2), which unites with some of the oxid of iron, forming a slag of ferrous silicate ($FeSiO_3$); the carbon escapes as carbon monoxid and dioxid; the phosphorus is also oxidized, and removed with the slag. As the impurities are gradually removed, the iron becomes less fluid, and the pasty mass is gathered on the ends of the stirring rods in masses of about

30 kg. These are removed from the furnace, hammered and rolled, and otherwise worked until each becomes a homogeneous mass of iron.

There are other methods of converting the cast iron into wrought or bar iron, such as melting the cast iron and blowing the air through it, or mixing the iron with pure ores and fusing, etc.; but all the methods aim at the removal of all the carbon but one-half per cent or less, and the complete removal of the other impurities. If we consider iron free from all impurities excepting carbon, it is found that the valuable properties of wrought iron — namely, forgeability, ductility, weldability, malleability, toughness, and softness — depend on the amount of carbon present. As the amount of carbon increases, the properties mentioned become less marked. When the amount of carbon has reached 2 per cent, these properties have practically disappeared. Toughness has become brittleness, and softness has become hardness. The melting-point has been lowered nearly to that of cast iron. Between the iron with less than .5 per cent and the same with 2 per cent of carbon, there are a great number of varieties in reference to the properties just mentioned.

One of the valuable properties of such iron is its hardness and its capacity to be tempered; that is, its capacity to have its hardness regulated within certain limits. This is called tempering. (See under STEEL.)

(*c*) **Steel.** — The iron described as containing from .5 per cent to 2 per cent of carbon, and possessing the property of being hardened and tempered, is called steel. Given, therefore, two samples of iron containing exactly the same per cent of carbon, their properties will not vary unless impurities are found in the one that are not in the other; or that these impurities are different in kind or in proportion. It is not true to say of steel that its character varies exactly according to the proportion of carbon present, unless steel which is pure iron and carbon is meant.

The problem then to be solved in the manufacture of steel from pig iron is to remove all that is possible of the other impurities and still have carbon present in the proper proportions. During the present century, up to the year 1860, nearly all the steel of commerce was made from wrought iron by adding sufficient carbon to it to make it contain the amount necessary to produce steel of the qualities desired. The process is dependent on the fact that iron when heated with charcoal to a high temperature (about 1100°) gradually takes up carbon, which penetrates to the centre of the iron bar. These bars are hammered and again rolled into bars, or they are broken up, remelted, and cast into ingots in order to make the steel homogeneous. It is then called cast steel. This process of the manufacture of steel is called the cementation process.

About 1860, the process of making a steel directly from the pig iron, known as the Bessemer process, began to supersede the cementation process, the products of which could be employed for many purposes. This process has undergone several interesting changes since it first came into use, but now consists essentially of removing the impurities in the iron by blowing air through melted pig iron held in a specially constructed crucible called a converter. The air oxidizes the carbon, silicon, etc., and consequently a rapid chemical action takes place in the converter, thoroughly agitating the mass of pig iron. The oxidation is carried on until all or nearly all of the carbon is oxidized. When the action is over, a calculated amount of pure "spiegeleisen" is added to the converter and thoroughly incorporated with the iron. The amount of spiegeleisen is determined by calculating how much will be necessary to furnish to the iron the required amount of carbon. A slight excess of the calculated amount is added. It was found early in the application of the Bessemer process, that it would not produce good steel, unless the pig iron was quite

free from all impurities except carbon, and perhaps silicon. This was especially true of pig iron that contained any notable amount of phosphorus or sulfur. It was found that the sulfur, phosphorus, and even silicon did not oxidize completely, and that steel made in this way was entirely useless for a great variety of purposes. The first improvement suggested was to carry the oxidation to completion, then add carbon to the iron as has been explained. The next improvement by which phosphorized iron could be converted into steel, was the addition of lime to the converter (usually to the lining), which readily combines with phosphorus oxid to form calcium phosphate. Manganese also serves an important function in removing the silicon. The immensely extended use of steel for structural purposes that has grown out of the adoption of the Bessemer process for its manufacture has encouraged the development of several other processes for its production. But the details of such processes carry us too far from the purposes of this work. Suffice it to say that all real progress has been made along the line of preparing a pure combination of carbon and iron, and the elimination of all other impurities. It is true that several valuable alloys have been produced such as the alloy of aluminum and iron, nickel and iron, chromium and iron, etc.

The tempering of steel, to which reference has been made, consists in heating the steel to a high temperature (usually red heat) and then suddenly cooling it. The steel is then carefully reheated and allowed to cool. This makes the hard brittle steel of the first cooling, softer and more elastic. The higher the temperature of the reheating, the softer is the cooled product. The temperature to which the hardened steel is to be heated and then cooled depends on the use to which it is to be put. The skilled workman has learned to decide when this temperature is reached, by observing the colors of the polished surface of the steel. These shades vary from pale yellow

through brown, purple, to deep blue; or it is heated to temperatures varying from 216° to 340°. In case of a thick mass of steel it requires a long time and careful heating to have the temperatures uniform throughout. In such cases the hard steel is dipped in hot oil or into molten alloys, usually an alloy of lead and tin, and left in the bath sufficiently long to become equally heated throughout. For example, watch springs must be very elastic and they are consequently heated until a polished surface becomes a deep blue, or to a temperature of about 310°. Hard drills are heated to 216° (pale straw color). The chemistry of these changes so far as the carbon and iron are concerned, is quite simple. In the suddenly cooled steel the carbon is combined with the iron, as is shown when such steel is dissolved in acids, the results of which have been previously described. In the slowly cooled steel, the carbon is mostly in the graphite form. The facts are illustrated in chill castings. As has been seen, the carbon of cast iron is usually more than is possessed by steel; consequently, if a casting is suddenly cooled on the surface, it becomes very hard, while the interior, which has cooled slowly, is fairly soft and tough. Castings for ploughs, etc., are made in this manner so that the wearing surface shall resist the action of the soil as the plough passes through it. Again, when wrought iron is heated in contact with carbonaceous matter for a short time, it takes up carbon to the extent of a thin layer, and when this iron is suddenly cooled, its surface becomes hard, while the interior is of soft and tough wrought iron. This is called case hardening.

The following table, showing the composition of various samples of the different kinds of iron, is taken from Jago's inorganic chemistry: —

Description.	Fe.	Mn.	Cu.	Carbon. Com- bined.	Carbon. Graph- ite.	Si.	S.	P.
Wrought Iron.								
Swedish	99.863	trace	—	0.054	—	0.028	0.055	trace
Russian	99.412	0.020	—	0.272	—	0.062	0.234	—
Welsh	97.720	—	—	—	—	0.260	0.210	0.710
Lowmoor	99.372	0.280	—	0.160	—	0.122	0.101	0.106
Steel.								
Rails	—	0.264	—	0.150		0.091	0.025	0.032
Boiler plate	—	0.273	—	0.300		0.056	0.040	0.041
Bessemer metal	—	0.576	0.025	0.490		0.009	0.033	0.036
Cast steel	—	—	—	0.950	0.220	—	—	—
Cement steel	98.093	—	—	1.807	—	0.100	—	—
Cement steel	—	0.120	—	0.627	0.102	0.030	0.005	0.000
Cast Iron.								
Gray iron	94.360	0.500	—	0.040	3.100	2.160	0.11	0.630
Charcoal, mottled	93.691	1.426	—	0.532	3.768	0.432	0.151	trace
Coke, hot blast, mottled	94.450	—	—	0.720	2.280	1.350	0.03	1.170
White iron	93.183	2.370	0.014	4.100	—	0.230	0.030	0.073
Spiegeleisen	88.560	5.750	0.160	5.040	—	0.410	0.08	0.000

Compounds of Iron.

Experimental Study, No. 21. — (Use the solution prepared in the previous study (*f*), (*g*), and (*h*), or prepare similar solutions from the salts of iron, using recently boiled water.)

(*a*) Treat solution (*f*) or (*h*) with the usual reagents, writing reactions and noting particularly the action of ammonium hydroxid, potassium ferro-, ferri-, and sulfo-cyanids.

(*b*) Treat the solution (*g*), the hot nitric acid solution (after driving off the excess of acid or neutralizing the acid with ammonium hydroxid), in the same way as in (*a*), noting and studying the action of the same reagents. Compare the results with those of (*a*). Let the precipitate formed with NH_4OH and a ferrous salt stand in the air for some time. Note and

explain changes. How can you distinguish one kind of iron from another? The precipitates are normal, except that soluble carbonates produce the hydroxids with ferric salts.

(*c*) Study the action of hydrogen sulfid and ammonium sulfid on a solution of a ferrous salt. Why is there but little precipitate formed with H_2S? Filter out the precipitate, and test for the free acid corresponding with the salt used. First drive off any H_2S present, unless the corresponding acid is volatile. Add a drop of acid to some of the original solution, and treat with H_2S. Explain. Add NH_4OH in excess to this solution, or add ammonium hydroxid to some of the original solution, and pass H_2S into it.

(*d*) Study the action of the same reagents on a ferric solution. What is the white precipitate produced with H_2S? Pass the gas for some time, warming the solution. Add $K_3Fe(CN)_6$ to a portion of it. Explain the result. Now add NH_4OH to the remainder of the solution. Filter out the precipitate, wash it, and dissolve in a little HCl, and test with $K_3Fe(CN)_6$. Explain and write the reactions. What element is reduced, and what one is oxidized? Write the reactions.

(*e*) To a solution of ferrous sulfate add a few drops of nitric acid (see under study of NITRIC ACID, Part I.) and warm, adding as long as the solution changes color, and neutralize the excess of acid. Treat the solution with both $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. What does this show? Explain fully the brown ring test for nitric acid. (See page 255, Part I.)

(*f*) Add H_2SO_4 to 20 cc. of a solution of ferric sulfate, and place in this several pieces of zinc. Allow the action to go on for say 20 minutes, and then test a portion of it with KCNS. Test another portion of it with $K_3Fe(CN)_6$. What changes have occurred? Would it make any difference whether the gas is passed into the solution or whether it be produced as just described? Explain your answer, and write the reactions.

(*g*) To a solution of ferric chlorid add $SnCl_2$. What kind

of an agent is stannous chlorid? Show what is the result of its actions in this case. In what condition is the tin? Prove it.

(*h*) To a solution of ferric chlorid add a solution of sodium thiosulfate, and warm. What is the precipitate? Warm for some time (not boil) and filter. Test the solution for sulfuric acid. In what condition is the iron? Prove it. Distil from the filtrate 10 cc. of liquid. Test it for hydrogen chlorid (free). From the substances formed, determine the reaction.

(*i*) To solutions of ferric and ferrous salts add solutions of tannic acid. Leave the mixture with the ferrous sulfate exposed to the air for some time. Explain result.

(*j*) Rub in a mortar some barium carbonate to a fine powder, adding water sufficient to make a thick cream-like mass. To a solution of ferric chlorid or nitrate add portions of this mass, noting all the changes. Warm, and add it as long as any action takes place, leaving a little of the carbonate in excess. What gas escapes? Filter out the solid matter, and test portions of the solution for iron. Where is it? How combined? Test the solution for a chlorid. With what is the chlorin combined? Dissolve the precipitate, and test for iron. Write the reactions. Test pure ferrous chlorid in this way. What will this fact enable you to do with the two kinds of iron?

(*k*) To a solution of ferrous salt add KCN, drop by drop, until an excess is added. Now add a little fixed alkali and warm. If any precipitate is formed, filter, and test portions of the filtrate with solutions of ferric salts. Study a ferric salt in the same way.

The reactions are: —

$$2\,KCN + FeCl_2 = Fe(CN)_2 + 2\,KCl;$$

$$Fe(CN)_2 + 4\,KCN = 4\,KCN.Fe(CN)_2 \text{ or } K_4Fe^{II}(CN)_6;$$

$$3\,KCN + FeCl_3 = Fe(CN)_3 + 3\,KCl;$$

$$Fe(CN)_3 + 3\,KCN = FeCN_3.3\,KCN, \text{ or } K_3Fe^{III}(CN)_6.$$

(*l*) To 10 cc. of ferric chlorid add 20 to 25 cc. of a solution of sodium acetate ($NaC_2H_3O_2$) and boil for a few minutes. A basic acetate of variable composition is formed. It finally becomes ferric hydroxid. Filter out the precipitate and test the filtrate for iron.

(*m*) To another 10 cc. of ferric chlorid add 20 cc. of sodium (or ammonium) acetate solution, and follow it with 4 or 5 cc. of sodium phosphate, a little acetic acid, and a few cubic centimetres of water. Boil the mixture, and filter out and wash the precipitate. Test portions of the filtrate for iron and phosphoric acid. Suspend the precipitate in a little water and add $(NH_4)_2S_2$, warm gently, and permit it to stand for a short time. Note the changes, and filter out the solid, and test the filtrate for phosphoric acid. What does this enable you to do in reference to phosphates? What is the use of the sodium acetate?

(*n*) Place some powdered iron sulfate in a crucible, and heat it gradually to a high temperature. Test the escaping product with moist blue litmus paper. What is left in the crucible? What has escaped?

(*o*) Make a borax bead and add a very little of a compound of iron. Heat in both the oxidizing and reducing flame and note changes in color. Tabulate the result in such a manner that the beads of other metals can be added in the table.

(*p*) Mix thoroughly 1 g. of iron oxid and 1.5 g. of potassium nitrate, and heat the mixture in an ignition-tube to low red heat. Cool, and treat the mixture with cold water. Filter, and treat a portion of the solution with $K_3Fe(CN)_6$. Heat another portion; what is the precipitate? What gas escapes? Filter, and dissolve the precipitate in HCl. Test for iron. What is its source? Test the filtrate with litmus. Explain. Also test for iron after it has been boiled for a few minutes. Write the reactions, considering K_2FeO_4 as formed in the first reaction.

(*q*) Fill the deflagrating spoon with borax mixed with a very little fine powdered iron oxid. Heat for a few minutes, and examine for the distinct particles of iron. What has become of the oxid? Use is made of the fact brought out here in welding. When two pieces of iron are heated until they become pasty, they can be united together by hammering or pressure if two chemically clean surfaces are brought together. Borax and other fluxing materials dissolve away the oxid that has been formed during the heating, and when the two pieces are hammered together, this flux is squeezed out, leaving the surfaces clean.

Compounds of Iron.

(*a*) **Oxids.** — According to the valence of iron it is possible at least to form two oxids; namely, $Fe^{II}O$ and $Fe^{III}{}_2O_3$. There is another oxid, having the formula Fe_3O_4, tri-ferric tetroxid, which is sometimes considered to be a combination of the two oxids, FeO and Fe_2O_3. When this oxid is dissolved in acid, the solution contains iron in both the ferrous and ferric conditions, and in the proportions indicated by the formula $FeO.Fe_2O_3$.

The compound produced in (*o*) corresponds to an oxid having the formula FeO_3; *i.e.* K_2FeO_4 corresponds to an acid of the formula H_2FeO_4, and this minus water is FeO_3. The acid has not been produced, the molecules being too unstable to exchange its potassium for hydrogen. When the change occurs in the potassium ferrate, KOH and $Fe.(OH)_3$, and oxygen are formed.

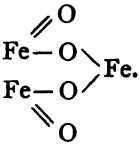
Ferrous oxid (FeO) is quite unstable in the air, taking up oxygen and becoming ferric oxid (Fe_2O_3). It is produced along with ferric oxid when iron is heated to a high temperature in the air. It can be prepared by heating ferric oxid (Fe_2O_3) to about 300° in an atmosphere of hydrogen. Many of the

ferrous salts, when ignited in a closed vessel, produce the black ferrous oxid; for example, ferrous oxalate, carbonate, sulfate, and the hydroxid. It is black powder soluble in acids. It is not found in nature except when it is combined with carbon dioxid, as ferrous carbonate or siderite.

Ferric oxid is found in nature in large quantities, and is known as hematite and specular iron ore. The specular ore is crystalline and has a brilliant metallic lustre. The hematite is sometimes black, sometimes red, and sometimes brown, and it is usually amorphous or only imperfectly crystalline. When any one of these ores is powdered, the result is always a red powder. When it is prepared from ferrous sulfate by decomposition by heating in the air, it is an amorphous red powder, called rouge, and is much used for polishing glass, metals, and also as a pigment. The native oxid is not readily soluble in acids, although when prepared in the wet way, it does easily dissolve in acid. It acquires this property of difficult solubility by heating to red heat. The old name for this compound is the sesquioxid of iron.

The oxid (Fe_3O_4) is called magnetic oxid. It is found in nature in many localities and is exceptionally free from impurities. The celebrated iron of Sweden and Norway is mostly produced from this ore. When ferric oxid is heated to a white heat, it loses oxygen and becomes the magnetic oxid. It is formed in many ways, *e.g.* when iron is heated to a high temperature in air, as in the case of the forging of iron at the blacksmith's anvil. Some native deposits of this ore have the property of the permanent magnet, and hence its name. It was called lædanstane, or loadstone, by the Anglo-Saxons, because of this property. This is the richest ore of iron, since, when it is pure, it contains 72 per cent of the metal. As has been said, this oxid contains both ferrous and ferric iron. It has been considered as a mixture of two oxids (FeO and Fe_2O_3), and also as a compound in which an atom of ferrous

iron unites two molecules of ferric iron as FeO_2; or it may be represented thus:



(*b*) **Hydroxids.** — The hydroxids of iron are all insoluble, and are produced in the usual way. Ferrous hydroxid ($Fe(OH)_2$) is easily oxidized in the air, and changes in color, as the oxidation progresses, from a grayish white through green gray to reddish brown, the color of the ferric hydroxid. The ferrous hydroxid is easily decomposed into water and ferrous oxid; *i.e.* the latter compound, provided it is heated away from oxygen. It is sufficiently basic to act upon litmus paper.

Normal ferric hydroxid exists in nature as limonite. This hydroxid gives up water readily, and nature furnishes several ores that are intermediate in composition between the normal compound and the ferric oxid, the product of its complete decomposition. Some of these intermediate compounds are:—

$$Fe_4O_3(OH)_6 \text{ or } 4\,Fe(OH)_3 = Fe_4O_3(OH)_6 + 3\,H_2O;$$

$$Fe_2O(OH)_4 \text{ or } 2\,Fe(OH)_3 = Fe_2O(OH)_4 + H_2O;$$

$$Fe_2O_2(OH)_2 \text{ or } 2\,Fe(OH)_3 = Fe_2O_2(OH)_2 + 2\,H_2O.$$

The first ore is known as limonite or brown hematite. It is an amorphous brown mass, usually quite compact. When deposited from chalybeate waters, it is more or less spongy and yellow in color. It is often produced when iron rusts in damp places. The second ore is known as bog iron ore, and is closely connected with limonite in origin. It is more or less porous in structure, and is non-crystalline. $Fe_2O_2(OH)_2$ is called göthite, and is crystalline in structure. Another hydroxid is called pyro-siderite, and is the meta-ferric hydroxid. It has the formula FeO.OH or $Fe\begin{matrix}=O\\-OH\end{matrix}$. It is formed from the

normal hydroxid by removing one molecule of water from one molecule of the hydroxid. It is sometimes spoken of as possessing acid properties; *i.e.* the hydrogen may be replaced by a metal, even by iron itself. (See MAGNETIC OXID, under ZINC FRANKLINITE.)

(*c*) **Salts of Iron;**[1] **Ferrous Chlorid ($FeCl_2$); Crystals ($FeCl_2.4\,H_2O$).** — Ferrous chlorid is a soluble unstable com-

[1] Before proceeding to study the salts of iron, it will be useful to notice the different methods by which salts have been produced and to bring together these and other general methods for their formation. The commercial manufacture of any particular salt will depend on the materials at hand, the relative cost of the various processes that may be employed, and the chemical character of the substances to be used. Necessarily not all the methods here given are of commercial importance. The methods for the formation of salts, including the basic compounds, may be classified as follows: —

(*a*) By the direct action of the non-metallic elements on metals.

(*b*) By the action of an acid on a metal.

(*c*) By the action of an acid on an oxid or a hydroxid.

(*d*) By the action of one salt on another.

(*e*) By the action of an acid on a salt.

(*f*) By special combinations of the preceding methods.

(*a*) The binary compounds (including salts) are often produced by the direct union of the non-metallic elements with the metals, sometimes with, and sometimes without, the aid of heat. Often the action is accompanied by much heat. For example, sulfur unites with iron only when it is heated to nearly red heat, but when the action begins, it produces sufficient heat to raise the temperature of the whole mass to the glowing point, and the action goes on without the aid of external heat. Again, when chlorin is brought in contact with sodium or potassium, the action begins, and continues without the addition of any heat. The principal compounds included here are those of the halogens and of sulfur (chlorids, bromids, iodids, fluorids, and the sulfids).

(*b*) The action of an acid on a metal depends on the solubility of the compound formed and upon the chemical relations between the acid and the metal. For example, hydrogen chlorid acts but little upon silver, since the chlorid when formed covers the surface of the silver, and this keeps the acid from contact with it. In other cases the salt that may be formed by other processes is not produced, since there is no action between the metal and the acid, even at quite high temperatures. For example, the action of sulfuric acid on bismuth is very slight at any temperature and is nothing at ordinary temperatures. The action of the stronger acids on metals has already been sufficiently discussed. With a few exceptions, the weaker acids do not generally have any action on the

pound which rapidly undergoes changes in the air, becoming oxidized to the ferric condition. In the presence of hydrogen chlorid, it becomes ferric chlorid ($FeCl_3$), and in the neutral solution both normal ferric chlorid and a basic ferrous salt

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metals. It has been noticed that copper is, to a certain extent, an exception to this general fact, owing to its property of slowly oxidizing in contact with air and moisture. The pure metal acted upon by the pure acid produces the pure salt, which may be separated by evaporating away the water and the excess of acid.

(*c*) The oxids are formed by the direct union of the metal and oxygen or by decomposing by heat the hydroxids, nitrates, or carbonates, generally, and in a few cases by decomposing the salts of other weak acids. The hydroxids are generally insoluble (see table of solubilities), and are produced by the action of a soluble hydroxid on soluble salts of the metals. Most of the hydroxids are sufficiently stable to be separated and dried without decomposition, some of the exceptions to which have been already noted. All of the metallic hydroxids and most of the oxids are decomposed by acids forming salts, even if they are insoluble when so produced. The native oxids and hydroxids are generally more insoluble in acids than are those produced by precipitation or than those that are produced by decomposition at low heat. It is probable that this is determined by the molecular condition or compactness due to conditions under which they were formed. This is illustrated by the fact that many of the oxids, notably the oxids of iron, when heated to a high temperature for some time, become quite insoluble. It is a general fact that state of division has much to do with chemical action. The more minutely divided any given matter is, the more rapid is its action upon any other matter with which it may be brought in contact, provided any action occurs under any state of division. This has been illustrated in the studies of lead and iron (lead tartrate). If the oxids or the hydroxids are pure, the desired salt can be obtained in the pure form by driving off the water and adding an excess of acid, redissolving, and crystallizing out the salt.

(*d*) This method of producing salt by the action of one salt on another is of quite general application. The general character of such actions has been sufficiently described on page 27. The more insoluble one of the products is, the more perfect is the reaction. Salts made in this way are, therefore, filtered out and washed free of the soluble substances and dried. Such salts are usually amorphous. The facts established as to the solubility of salts enable one to decide what salts can be prepared in this way.

(*e*) This method of producing salts is applicable when the desired salt (of the acid used) is insoluble, and when a soluble salt containing the metal can be obtained. For example, when lead nitrate is treated with sulfuric acid, lead sulfate, insoluble, is formed, and nitric acid is set free. The insoluble salt can be

($FeCl_3$ and FeOHCl) are formed. It is readily oxidized by chlorin, nitric acid, and most of the other oxidizing agents. Prepared in the dry way, by the action of dry hydrogen chlorid on powdered iron, it is a volatile white solid. Its

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separated by filtering and washing the precipitate. This method is not of wide applicability, since often the salt that may be formed is dissolved in the acid set free by the action, and an equilibrium between the parts of the system is thus established. For example, ferrous sulfid is insoluble, and, on general principles, it should be precipitated when a soluble salt of ferrous iron is acted upon by hydrogen sulfid. Examine the case when hydrogen sulfid acts on ferrous sulfate.

$$FeSO_4 + H_2S = FeS + H_2SO_4.$$

Ferrous sulfid is readily decomposed by sulfuric acid, and when a sufficient amount is produced by the action of hydrogen sulfid on the ferrous sulfate, it decomposes any sulfid as fast as it is formed; or, in other words, an equilibrium is soon reached, and no more sulfid is precipitated. A case in point here is that of the second group of metals. The sulfids of this group are not soluble at all, or are so only in concentrated hydrochloric acid, hence they are all precipitated by hydrogen sulfid from a dilute acid (HCl) solution. The sulfids of the third and fourth group of metals, as we shall see later, are all soluble in hydrochloric acid, and consequently the addition of a little of the acid completely prevents their precipitation.

Again, such salts as the carbonates, nitrates, and the halides, etc., are decomposed by certain acids producing volatile products, which can be driven off by heat, and the metal combined with the radical of the decomposing acid is left in solution or as a non-volatile residue. The action of sulfuric acid on sodium chlorid or nitrate in producing the corresponding acids is a common example of this action.

Particular use is made of the carbonates of metals for producing other salts, since the carbonates are easily produced, are often found native, and are generally insoluble; and also the products of the decomposition, water and carbon dioxid, are readily driven off by heat, thus leaving the pure salt. The carbonates are generally decomposed even by the so-called weak acids. For example, lead carbonate is readily decomposed by acetic acid according to the reaction—

$$2\,PbCO_3.Pb(OH)_2 + 6\,HC_2H_3O_2 = 3\,Pb(C_2H_3O_2)_2 + 4\,H_2O + 2\,CO_2.$$

If an excess of the carbonate is used, the acid and the carbonate being heated (in many cases), the excess of acid is thereby avoided and the insoluble excess of the carbonate filtered out; the new compound is left a pure salt in solution in water, provided the salt that is formed is soluble.

(*f*) Special cases are those in which the substances from which the salt is to

vapor density at white heat corresponds to the molecule $FeCl_2$; but at lower temperatures, the molecule is double this one, or Fe_2Cl_4. It forms double chlorids of the form R_2FeCl_4.

Ferric Chlorid ($FeCl_3$); Crystals ($FeCl_3.6H_2O$). — Ferric chlorid is formed by the direct union of chlorin and iron. When so prepared, it is quite black in color, forming in scales as it sublimes. The salt is quite deliquescent. It vaporizes at about 450°, and at this temperature it has a density corresponding closely to the molecule Fe_2Cl_6. Higher temperatures decompose the molecule, but the density of the vapor has not been satisfactorily settled. It probably corresponds to the molecule $FeCl_3$. An interesting property of the ferric chlorid is its power to dissolve ferric hydroxid. Use is made of this property in making a medicinal iron preparation called tincture of iron.

Ferrous Iodid (FeI_2); Crystals ($FeI_2.4H_2O$). — This compound, like the corresponding chlorid, decomposes when its solution is exposed to the air, the iodin is set free, and ferric

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be formed are conditioned in such a manner that a combination of some of the previous methods is necessary in order to produce the pure salt. The facts can be best shown by an illustration.

Suppose it is necessary to form ferric chlorid, having given ferric sulfate and sodium chlorid; *i.e.* the iron is to come from ferric sulfate, and the chlorin from sodium chlorid. The salt required is soluble, and thus the substances from which it is to be formed will not produce the chlorid by the action of one salt on the other in a way that it can be separated. We do know that hydrochloric acid will dissolve the hydroxid and form ferric chlorid. Consequently, the hydroxid is produced by means of ammonium hydroxid, and hydrogen chlorid by the action of sulfuric acid on common salt. Now the hydroxid having been thoroughly washed, to free it from reagents, it is dissolved by the acid produced from the chlorid.

It is a most valuable exercise for the student, as the work progresses, to solve problems like the preceding, and others, on the other methods of preparing salts that may be arranged by the instructor. All reactions, etc., should be carefully written and placed in a note-book.

Hereafter, the preparation of salts will not be given unless it involves some peculiarities not given in the preceding methods.

hydroxid is formed. It is used in medicine, and is made by grinding the iodin and iron together in presence of water free from dissolved oxygen.

Ferrous Sulfate ($FeSO_4$); Crystals ($FeSO_4.7\,H_2O$). — Ferrous sulfate is one of the most important salts of iron. It is a very soluble crystalline substance called green vitriol (or copperas), because of its green transparent crystals. It gives up its water of crystallization completely at 300°, although all but one molecule escapes at 100°. The dehydrated salt is a white powder. When the salt is heated to redness, it is decomposed into ferrous oxid (or ferric oxid, if heated in air) and sulfur dioxid and trioxid. It is used to prepare Nordhausen or pyro-sulfuric acid, by allowing the latter to oxidize in the air. This is partially dried and heated, when this reaction occurs: —

$$FeSO_4.H_2O = H_2S_2O_7 + SO_2 + Fe_2O_3.$$

$$2\,FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

The ferric oxid thus produced is used as a polishing powder. The sulfate is used as a deodorizer and disinfectant agent for making inks, in dyeing, and for tanning. A use in dyeing is shown in (*a*) by the production of Prussian blue, when a ferrous salt is treated with potassium ferri-cyanid. It is also used in purifying coal gas.

Ferrous sulfate forms double salts, especially with the alkali sulfates. They crystallize out of their mixed solutions one molecule of the iron sulfate for each molecule of the alkali sulfate. They all contain six molecules of water. These double salts are more stable than is the iron sulfate by itself. This salt is often included with the alums. (See under ALUMINIUM.) Ferrous sulfate forms an unstable brownish to black compound with nitric oxid (NO), which fact is used in the "brown ring test" (which see).

Ferric Sulfate ($Fe_2(SO_4)_3$). — Ferric sulfate is of interest because of its capacity to form double salts with the alkaline

sulfates. They have the form $M_2SO_4.Fe_2(SO_4)_3\ 24\ H_2O$, and are classed with the alums.

The ferric sulfate is produced by oxidizing the ferrous sulfate by the usual methods.

Iron Sulfids. — Ferrous sulfid is an insoluble black substance, and is an example of a ferrous compound that is more stable than is a ferric compound. Ferric sulfid is not readily formed, and is a very unstable compound. Ferrous sulfid is soluble in hydrochloric and other acids, and consequently cannot be precipitated from solutions of ferrous salts. It is not soluble in acetic acid, and can be precipitated from solutions of ferrous acetate.

The native sulfid contains twice as much sulfur as the ferrous sulfid, and has the formula FeS_2. It occurs in nature in large, brass-yellow crystalline masses, and is widely distributed. When this sulfid is heated away from air, one-half of the sulfur is driven off, and ferrous sulfid is left. Heated in the air, the sulfur is oxidized, as is usual with metallic sulfids. The abundance of this sulfid makes it useful in preparing sulfuric acid. How? The ferric oxid left has been used as a source of iron, but is used principally as a polishing-powder called rouge.

Ferric sulfid (Fe_2S_3) corresponds to ferric oxid (Fe_2O_3), and is not produced by the action of a soluble sulfid on a ferric salt. Under these conditions, the iron is reduced, and sulfur is set free. It is produced by heating ferrous sulfid with sulfur.

One other sulfid is known having the formula (Fe_2S_4), corresponding to magnetic oxid (Fe_2O_3). This sulfid is magnetic.

The Iron Cyanids. — In the last study a method for preparing the cyanid compounds has been illustrated. Many of the normal cyanids are insoluble in water, but are soluble in an excess of the reagent, potassium cyanid (KCN), which is commonly used to precipitate them. The products, the double cyanids, in the case of the iron compounds, are stable compounds in which the iron does not present the same properties

that it does in its ordinary combinations; that is, it is not precipitated by the usual reagents. These compounds are represented by the formulæ $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, and are named potassium ferro-cyanid and potassium ferri-cyanid respectively. This potassium can be replaced by other metals without changing the remainder of the molecules, many of which compounds are very stable. The salts produced with each form of iron are quite characteristic, especially that produced with ferrous and the potassium ferri-cyanid, and that produced with ferric iron and potassium ferro-cyanid. The first compound is called Turnbull's blue, and the second Prussian blue. The formulæ are $Fe_3(Fe(CN)_6)^{III}_2$ and $Fe_4(Fe(CN)_6)^{IV}_3$, or ferrous ferri-cyanid and ferric ferro-cyanid. When ferro-cyanid is treated with a solution of a ferrous salt, one-half of the potassium is replaced by iron, producing a white precipitate which turns blue on exposure to the air, owing to its change to Prussian blue. Ferric ferri-cyanid has not been separated. When a solution of ferri-cyanid is treated with a solution of a ferric salt, the original solution becomes olive-brown. The action is characteristic for ferric salts. The presence of small amounts of a ferrous salt is readily detected by this action. The blue precipitate produced with the ferrous iron can be seen in the liquid, especially after it has been diluted. The potassium of potassium ferro- and ferri-cyanids has been replaced by hydrogen, which can in turn be replaced by metals. The two hydrogen compounds are called hydrogen ferro- and ferri-cyanids, or ferro- and ferri-cyanic acids. These compounds are decomposed by the fixed alkali hydroxids at boiling temperatures, producing ferrous or ferric hydroxid (according to which cyanid is acted upon) and the alkali cyanids.

Potassium ferro-cyanid is easily oxidized to ferri-cyanid. This is commonly done by the means of chlorin. The chlorin removes one atom of potassium and forms potassium chlorid. The iron is oxidized, as can be shown by the usual test and by the action of boiling potassium hydroxid.

Potassium ferro-cyanid ($K_4Fe(CN)_6.3H_2O$) is the most important of the cyanids, since it is the starting-point in the manufacture of most of the other related compounds. It is made by heating together potassium carbonate and nitrogenous animal matter, such as blood, horns, hoofs, etc. By this reaction potassium cyanid is formed, which reacts with iron or with iron compounds (Fe_2O_3) that are added at the same time. If iron is added, an intermediate compound is usually formed with the sulfur of the organic matter which is decomposed, and the ferro-cyanid is produced. The compound loses its water of crystallization at 100°, and decomposes at red heat into potassium cyanid and carbid of iron (FeC_2).

Potassium ferro-cyanid, or yellow prussiate of potash, is the source of the Prussian blue used in dyeing, for paints, and pigments.

The process of dyeing is quite simple in principle. The goods to be dyed are dipped in a solution of ferric salts, and when it is saturated with the solution they are transferred to a solution of potassium ferro-cyanid. The blue is deposited in the fabric as a solid. An excess of the ferric salt must be used, since an excess of the ferro-cyanid produces a compound in which one atom of potassium is not replaced. The compound is $KFe(CN)_6$, and since it is soluble, it is called soluble Prussian blue. Potassium ferri-cyanid forms the same compound with ferrous salts ($FeCl_2$).

Ferrous Carbonate ($FeCO_3$). — This compound occurs in nature, and is known as siderite. It is soluble in water charged with carbon dioxid, and consequently is found in many natural waters. Such waters are called chalybeate waters. When these waters come to the surface of the earth in the form of springs, the carbon dioxid escapes (in part at least), and the normal carbonate being insoluble is deposited, which in turn is oxidized and decomposed in presence of the water, leaving a deposit of ferric hydroxid.

Siderite, or spathic iron ore, is abundant, and is one of the principal sources of iron. Most of the English ore is of this kind. The carbonate is often mixed with clay in nature, and is then called clay iron ore.

Ferric carbonate is not known. The basic character of the hydroxid of iron is not sufficiently strong for it to form a salt with weak acid, as carbonic acid. When a ferric salt like ferric sulfate ($Fe_2(SO_4)_3$) is acted upon by a soluble carbonate, ferric hydroxid ($Fe(OH)_3$) is produced, instead of the carbonate.

The other salts of iron are of little importance except in analytical chemistry, the facts in reference to which have been developed in the experimental study. Ferrous silicate ($FeSiO_3$) is of importance in metallurgy, since it fuses quite readily and aids in removing impurities from iron ores.

Oxidation and Reduction of Iron. — Iron, like all the elements having a variable valence, is both an oxidizing and a reducing agent. The most stable compounds of iron correspond to ferric oxid (Fe_2O_3). Although the higher oxid (FeO_3) can be produced, as was seen in the compound K_2FeO_4, it requires the presence of a strong base like potassium to aid the iron in holding this amount of oxygen. But when this compound is decomposed, oxygen is set free, and the iron returns to the ferric condition represented by Fe_2O_3. Most of the compounds of iron, therefore, contain iron either in the ferrous or ferric condition. It acts, therefore, more powerfully as a reducing agent than it does as an oxidizing agent.

The ferrous compounds, in solution, are changed in the air to ferric compounds. If there is no free acid present, two salts are usually formed; namely, a normal and a basic salt. For example, ferrous chlorid undergoes the following changes:

$$4\,FeCl_2 + O_2 + 2\,H_2O = 2\,FeCl_3 + 2\,Fe\begin{<}{OH}{Cl}\text{.}$$

Ferrous sulfate undergoes similar changes:

$$12\,FeSO_4 + 6\,H_2O + 3\,O_2 = 4\,Fe_2(SO_4)_3 + 4\,Fe(OH)_3.$$

If an acid is present, the iron is all in the form of a ferric salt. Oxidizing agents like nitric acid, chlorin, and the higher oxids of many of the metallic elements such as chromic oxid (CrO_3,Mn_2O_7), etc., readily oxidize the metal. (See under these metals.) An acid must be present to dissolve the metallic oxids that are formed.

Reducing agents, although less readily, change the ferric salt back to the ferrous "conditions"; such agents as hydrogen sulfid, nascent hydrogen, stannous chlorid, and sodium thiosulfate produce this change.

CHROMIUM.

Occurrence and Distribution. — Chromium does not occur free in nature, but is found combined, principally as crocoisite, lead chromate ($PbCrO_4$), and chrome iron ore ($FeOCr_2O_3$). It is not widely distributed, nor does it occur in large quantities. It is found in the United States, principally in California. In Europe, its ores are found in Hungary, the Ural Mountains, and in Sweden and Norway. Asia Minor furnishes a large per cent of the chromium of commerce. It is found in very small quantities in certain minerals, imparting to them characteristic colors. The emerald and serpentine are examples of such minerals.

Preparation. — Chromium is practically all produced from the chrome iron ore, which is a combination of the two oxids of chromium, Cr_2O_3 and ferrous oxid. To prepare the metal involves the removal of the iron and oxygen. The metal, until recently, has not been used except as laboratory speci-

mens, although its compounds are employed in many ways. The source of its compounds is the oxid (CrO_3), formed by oxidizing chrome iron. An alloy of iron, chromium, and manganese is also prepared.

When the pure metal is desired, it is prepared from the oxid by reducing it with carbon. The chemistry of this process is very simple, and consists in the removal of the oxygen by combining it with carbon. The physical difficulties of the process are more serious, since the temperature required for the reduction is greater than that of the ordinary blast furnace. The oxid is mixed with a rich carbonaceous substance like sugar, and heated in a furnace similar to the one used in the preparation of platinum, when the metal is set free and fused. The metal is also prepared by decomposing chromium chlorid by electrolysis, or by means of sodium amalgam. Zinc also sets the metal free from its chlorid. The oxid is prepared by fusing and oxidizing the chrome iron with a mixture of potassium hydroxid, calcium oxid, or lime (soda lime) and potassium nitrate.

The iron becomes oxidized to ferric oxid (Fe_2O_3), and the chromium becomes CrO_3 (corresponding to FeO_3), combined with calcium and potassium, as calcium and potassium chromates ($CaCrO_4$ and K_2CrO_4).

The reaction is: —

$$6\,FeO.Cr_2O_3 + 14\,KNO_3 + 10\,KOH\,(+CaO) = 3\,Fe_2O_3 + 12\,K_2CrO_4 + 5\,H_2O + 14\,NO.$$

The potassium chromate (see under CHROMATES) is soluble in water, and is dissolved out of the fused mass. The solution is concentrated and treated with sulfuric acid, which removes the base from the chromate, and sets the oxid free.

$$K_2CrO_4 + H_2SO_4 = K_2SO_4 + CrO_3 + H_2O.$$

It is usual, when the oxid is manufactured on the commercial scale, to mix the powder ore with chalk (calcium carbonate,

which heat decomposes into CaO and CO_2; see under CALCIUM OXID), and to heat it in a reverberatory furnace. The carbon dioxid escapes from the chalk and renders the mass porous, and this permits the air to permeate all parts of the mixture. The oxygen of the air takes the place of the potassium nitrate in the reaction just given, and the lime unites with the chromium trioxid to form calcium chromate ($CaCrO_4$). The mass is broken up and washed, and the clear concentrated solution of the calcium chromate is treated with concentrated sulfuric acid, which sets the oxid (CrO_3) free.

An alloy of iron and chromium, containing from 30 to 60 per cent of chromium, is made by reducing the chrome ore at such a temperature that the iron fuses with the chromium. Such an alloy is used in making chrome steel, a very valuable alloy of iron and chromium. It is added to the molten steel in quantity to give to it a calculated amount of chromium.

Physical Properties.[1] — Chromium is a very hard substance, and is the most difficultly fusible of all the metals. It is crystalline in structure, the form of which depends on the method used in its production. When obtained by ignition methods, it crystallizes in rhombohedra. When deposited by electrolysis, it is in the form of crystalline scales or plates. The metal has a slight metallic lustre, and is steel-gray in color. The descriptions of the metal given by different observers differ quite widely. Some describe the crystals as tin-white.

Chemical Properties. — The element chromium forms stable compounds, but is not very readily attacked by any other element. It does not oxidize in the air at ordinary temperatures, and it is only slowly acted upon at higher temperatures. At the highest temperatures that can be produced it oxidizes rapidly. The metal is oxidized by heating with such oxidizers

[1] The study of the metal is omitted, owing to the fact that the free metal is of but little practical importance, and its use is mostly confined to its compounds.

as the nitrates and chlorates. It dissolves readily in hydrochloric acid, and quite easily in hot sulfuric acid.

Nitric acid does not attack the metal. (Compare with action of nitric acid on the other metals.) Advantage is taken of this fact in preparing the metal from its chlorid by fusing it with zinc. The separated metal alloys itself with the zinc, from which it is removed by nitric acid, which readily dissolves the zinc.

Chromium combines readily with chlorin and iodin at raised temperatures.

Name, History, and Uses. — Chromium was first separated and studied by Vauquelin and Klaproth in 1797. They obtained it from crocoisite, or native lead chromate ($PbCrO_4$). The metal has been studied since then by several investigators, such as Deville and Bunsen. Within a few years its effect on the properties of steel has been noted, and processes for its preparation have been developed. It renders the unhardened steel tough, and at the same time it can be made very hard. It is often combined or welded to wrought iron, thus making bars or sheets that are difficult to cut or to bend. The amount of chromium in the steel varies from about 1 per cent to 4 or 5 per cent. Chrome steel is used for making cutting instruments that must be very hard. For example, it is used to make instruments for cutting ordinary steel, for cutting glass, and for sharpening knives. The name *chromium* was given to the metal by Vauquelin, because of the color of its compounds.

Atomic Mass and Valence. — At least one volatile compound containing chromium is known. It is a compound of chromium, oxygen, and chlorin (see page 179). This compound shows on analysis 52.2 parts of chromium, 31.92 parts of oxygen, and 70.74 parts of chlorin. The two chlorids (chromous and chromic) of the metal contain 52.2 parts of chromium combined with 70.74 parts, and 106.11 parts of chlorin respectively. On the basis of chlorin 35.37, or oxygen 15.96, the smallest amount

of chromium found in any of the molecules that have been studied is 52.2. All other proportions are multiples of this number.

The specific heat of chromium gives a result, according to the law of Dulong and Petit, very close to this number, 52.2. Its atomic mass is, therefore, 52.2.

The valence of the element as shown by its two chlorids is 2 and 3, or it is the same as that of iron. It forms another class of compounds in which the chromium is a hexad. The oxids of chromium are, therefore, CrO, Cr_2O_3, and CrO_3.

Experimental Study, No. 22.—(Material: unignited chromic oxid (Cr_2O_3) and potassium chromate. The ignited oxid is not soluble in acid, or only very slowly soluble. Solution of a chromic salt may be furnished instead of the oxid.)

(*a*) Dissolve a few grammes of the oxid in hydrochloric acid, neutralize most of the excess of acid, or use an excess of the oxid. (There should not be an excess of acid.) Write the reactions.

(*b*) Study this solution in the usual way with the usual reagents, noting colors of precipitates and writing the reactions. Note the effect of boiling the solution in excess of the fixed alkali hydroxid. The carbonates, cyanids, and ammonium sulfid precipitate the hydroxid. H_2S does not react with basic chromium.

(*c*) Examine the solution of the chromate in the same way; *i.e.* examine sufficiently to determine the comparative reactions of these reagents on the solutions of the two classes of compounds.

(*d*) Study the action of solutions of the following substances on portions of the chromate solutions: $BaCl_2$, $AgNO_3$, $Pb(C_2H_3O_2)_2$, and $HgCl_2$. Write reactions, and note colors of precipitates.

(*e*) To 20 cc. of a solution of chromium salt, say $Cr_2(SO_4)_3$, add NH_4OH to slight excess. Heat to boiling, and filter out

the hydroxid. Transfer a portion of this precipitate to a piece of platinum foil, and mix with it about equal volumes of potassium nitrate and potassium carbonate. Heat the mass to quiet fusion. (Be sure of this fusion.) When the foil is cold, place it and its contents in a beaker, and cover with water and warm. Filter (if necessary), and acidify with acetic acid. Warm to drive off carbon dioxid, and test with the reagents mentioned in (*d*), especially with $Pb(C_2H_3O_2)_2$.

$$Cr(OH)_3 + KNO_3 + K_2CO_3 = K_2CrO_4 \text{ (or } K_2O.CrO_3) + NO + CO_2 + H_2O.$$

Balance this equation, and explain the use of each factor. Why is the acetic acid added to the filtrate? Compare with the reactions given under the preparation of the element. What is the color of the fused mass? This is a delicate test for chromium in the basic form. Under the same conditions is iron oxidized? Suppose the hydroxid of iron is mixed with the chromic hydroxid, in what condition is it when the fusion is finished? Is the product soluble? Could you separate and recognize iron and chromium (basic) in this manner? Explain.

(*f*) Make a saturated solution of potassium dichromate, and to 20 cc. of it add 20 cc. of concentrated H_2SO_4. Allow the mixture to cool, and note the crystals that form. Loosely plug a funnel with asbestos, and filter out the crystals. Remove some of the crystals, and add water to them. Follow with KOH. Note the color of the solutions. Compare with the original solution. Compare with the solution of the normal chromate (K_2CrO_4). Add a few drops of sulfuric acid to a solution of the normal chromate. Evaporate the solution, and compare the solid with the dichromate. The crystals are CrO_3, chromium trioxid.

(In the manufacture of the metal it was noticed that the trioxid was produced. Generally, however, the calcium chro-

mate ($CaCrO_4$) which is formed is treated with sulfuric acid, which forms soluble $CaCr_2O_7$. To this solution is added potassium sulfate, which forms potassium dichromate ($K_2Cr_2O_7$), and sparingly soluble calcium sulfate ($CaSO_4$), which is filtered out, and the solution is concentrated, and dichromate is crystallized out. This compound is the source of all the compounds of chromium. From this compound the trioxid can be produced by adding sulfuric acid to the saturated solution according to the method just given.)

(*g*) Dissolve a few crystals of the trioxid in 10 cc. of water (acidify with HCl) and add 1 cc. of hydrogen peroxid, or add barium dioxid instead of the hydrogen dioxid. Note the color. Add ether and shake well. What gas escapes? It is supposed that an oxid having the formula Cr_2O_7 is formed, which produces the colored solution.

(*h*) Pass H_2S through a solution of the trioxid acidified with HCl. Note and explain the change of color of the solution, and also the precipitate formed. Pass the gas for 10 to 20 minutes, and then warm the solution slowly, and finally boil until the excess of H_2S has been driven off. How can you prove whether the oxid is all changed? (See (*d*).) Test the solution (filtered) with NH_4OH. In what condition is the chromium now? What was the acid added for? Evaporate a little of the solution (say 5 cc.) to dryness so that all the excess of acid is driven off. Redissolve, and test for hydrogen chlorid. Where is the sulfur? Test for sulfuric acid. What does this show as to the combination of the chromium. Suppose the dichromate had been used, show what the products are. Write the reactions in both cases.

(*i*) Into a hot solution of the dichromate (or chromate) pass SO_2, and note changes as in (*h*). Pass the gas until the changes are complete. Boil to drive off excess of SO_2. Test for sulfuric acid. Write the reactions. How is the chromium combined now? Prove it. Add a few drops of sulfuric acid

to the solution. Note and explain the changes produced by the acids after writing and studying the first reaction.

(*j*) To a solution of the normal chromate (K_2CrO_4) add the trioxid. Evaporate the solution, and compare the residue with $K_2Cr_2O_7$ and with K_2CrO_4.

(*k*) Add KOH to 20 cc. of a solution of $K_2Cr_2O_7$ so long as the color changes. Evaporate to dryness. Same comparison as (*i*).

(*l*) Place a few grammes of chromium trioxid in a test-tube and gradually heat to high temperature. Test the escaping gas with a burning stick. Cr_2O_3 is left. Write the reaction.

(*m*) Add concentrated HCl to 2 or 3 g. of the trioxid. Warm, and note the gas that escapes. What is its source? Make a portion of the solution alkaline with NH_4OH. In what condition is the chromium now? Evaporate the remainder of solution to crystallization. From this result how would you expect HCl to act on potassium dichromate ($K_2Cr_2O_7$)? Write reactions and explain.

(*n*) Add 10 cc. of sulfuric acid to 4 or 5 g. of $K_2Cr_2O_7$ and warm. To a portion of the product add a few crystals of any chlorid, *e.g.* common salt. The gas that escapes has been found by analysis to be correctly represented by the formula CrO_2Cl_2. The formation of this substance is characteristic for chlorids or for chromates, under the conditions given. Pass this gas into say 10 cc. of NH_4OH. Add sufficient acetic acid to a portion of this alkaline solution to neutralize it and then add $Pb(C_2H_3O_2)_2$. Compare with (*d*). In what condition is the chromium? (A little care is necessary in passing over the gas. It is heavy, and requires heat to force it out of the tube. A solution of chlorid cannot be used in this test; the chlorid must be in the solid form.)

How does the first action differ from that in (*m*)? Why is the H_2SO_4 necessarily present since CrO_3 is present in both cases? Water decomposes the chromium dioxy-dichlorid,

and if it is present, the gas is not produced in sufficient quantities for further testing. Write all the reactions. This characteristic action is often used to recognize chlorids in presence of bromids.

Bromids under these conditions give a brown gas from the decomposition of the bromid, but when the gas is passed into NH_4OH, the solution does not give the characteristic test of a chromate.

Although this test for a chlorid or for a chromate is not particularly delicate, it is a very characteristic one.

(*o*) Make a borax bead and add a little chromium compound like the hydroxid. Heat in both the reducing and the oxidizing flames. Note the color of the bead and write the reaction.

(*p*) Fuse 5 g. of $K_2Cr_2O_7$ with 1.5 g. of sulfur. Heat until the action is complete. Cool and powder the mass, and treat with water and filter. The green residue is chromic oxid (Cr_2O_3). Test the solution for sulfuric acid. Where is the potassium? Write the reaction and explain.

Compounds of Chromium.

(*a*) **Oxids.** — Chromium forms three and possibly four oxids. They are represented by the formulæ CrO, Cr_2O_3, CrO_3, and Cr_2O_7, and are named chromous, chromic, chromic anhydrid or the trioxid, and perchromic anhydrid.

Chromous oxid has not been separated from its hydroxid. When this hydroxid is heated away from air, instead of decomposing and forming chromous oxid and water, as is usual with metallic hydroxids, it decomposes thus: —

$$2\,Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

Chromic oxid (sesquioxid) is the most stable of the oxids of chromium. It can be prepared in the usual manner. (See

under HYDROXIDS.) It is also prepared by fusing potassium dichromate with sulfur. The dichromate is reduced, and the sulfur is oxidized, forming potassium sulfate. The oxid fuses at very high temperatures, and when cooled it forms a substance so hard that it may be used to cut glass. When fused with borax or with silicates (or glass), it unites with them, forming emerald-green compounds. It is often used to impart green tints to glass and porcelain, and is employed as a pigment in oil and china painting.

It is insoluble in water and in most of the acids. When heated in sulfuric acid, it slowly forms the sulfate. If the powder has been thoroughly ignited, it is not dissolved in any acid. Alkalis dissolve it, forming the alkali chromates if the mixture is heated in the air.

Chromium trioxid (CrO_3) is produced by decomposing the alkali chromate, or from the dichromates, by sulfuric acid. The chromates are produced by the oxidation of chromic oxid (Cr_2O_3) in presence of alkalis. (See under CHROMATES.)

The trioxid is quite soluble in water, forming solutions that are acid to litmus. The compound formed with water is not sufficiently stable to permit its separation from the excess of water. The solid oxid is set free under these conditions. The trioxid is a red crystalline solid that melts at 193°, and is decomposed at 250° into chromic oxid (Cr_2O_3) and oxygen. It is therefore less stable than is the chromic oxid. The trioxid and the salts of its acid are among the most active oxidizing agents, and in nearly all cases they return to the chromic oxid form. The oxidation of inorganic substances requires the presence of an acid to unite with the basic chromium, and in case of the chromate to unite with the base combined with chromic acid.

The perchromic oxid (Cr_2O_7) has not been isolated and examined with sufficient care for many of its properties to be known. It is supposed to be formed when (dissolved in water)

the trioxid in solution (or a chromate) is treated with such a powerful oxidizer as hydrogen dioxid. Under these conditions a deep blue solution is produced, which, however, is soon decomposed, oxygen escapes, and if an acid is present, the chromium becomes basic, and a salt of the acid used is formed. This compound is soluble in ether, and is more stable while held in this solution. It imparts the blue color to the ether. When, therefore, a solution is treated with hydrogen dioxid, and this color is produced, but rapidly disappears, it is considered as satisfactory evidence that hexad chromium is present. It is a delicate and characteristic test for chromium in this condition. A blue color is produced if the solution contains only 1 part of chromate dissolved in 40,000 parts of water.

(*b*) **Chromium Hydroxid.** — Chromous hydroxid is, like chromous oxid, very easily oxidized in the air. It oxidizes more readily than does the corresponding hydroxid of iron. In the absence of air or of oxidizers it is decomposed, and the chromium is oxidized to Cr_2O_3, as previously given under the oxid. Acid dissolves it, forming the corresponding chromous salts.

Chromic hydroxid, like chromic oxid, is the most stable of the hydroxids, and is basic in character, forming salts with many of the acids. It is, however, dissolved in excess of alkali hydroxids, forming unstable compounds called chromites, having the form $KO - Cr = O$.

The alkali chromites are decomposed at boiling temperatures, most of the chromium being deposited as the hydroxid.

Another basic hydroxid is produced by fusing potassium dichromate in boric oxid (B_2O_3). The heat in connection with the boric oxid (B_2O_3) decomposes the chromate, forming potassium and chromium borates and setting oxygen free. When this mass is broken up and treated with water, which dissolves the potassium borate and decomposes the chromium borate, an insoluble residue separates out. When this is dried,

it is found to contain $Cr_2O_3.2\,H_2O$ or $Cr_2O.(OH)_4$. The reactions may be represented thus: —

$$4\,B_2O_3 + K_2Cr_2O_7 = 2\,KBO_2 + 2\,Cr(BO_2)_3 + 3\,O;$$
$$2\,Cr(BO_2)_3 + 11\,H_2O = 6\,H_3BO_3 + Cr_2O(OH)_4.$$

The solid, called Guignet's green, is a beautiful green pigment, is not poisonous, and is not acted upon by light and chemical agents generally. It therefore takes the place of the poisonous green pigments like Paris and Schweinfurt's greens.

The hydroxid ($CrO_2(OH)_2$) is not produced by the action of an alkali hydroxid on a salt of chromium. Its actual formation is only inferred from the compounds that are formed with metals which have the form R_2CrO_4 or $CrO_2(OR)_2$. It is acid in character, and forms stable salts with many of the metals. In these salts, called chromates (which see), the chromium does not behave as it does in the ordinary salts of chromium. It is not precipitated by the reagents that form precipitates with chromium salts.

Chromyl Dichlorid. — When chromium trioxid is heated with a chlorid in the presence of sulfuric acid, a compound is formed which distils over, having the formula CrO_2Cl_2, as determined by its quantitative analysis and vapor density. This compound is called chromium dioxy-dichlorid, or chromyl dichlorid. It is chromic acid in which two molecules of hydroxyl are replaced by chlorin, or it may be regarded as the trioxid in which an atom of oxygen is replaced by a corresponding amount of chlorin. With water it is decomposed, forming hydrogen chlorid and chromic acid. (See under the DICHROMATE.)

$$CrO_2Cl_2 + 2\,H_2O = CrO(OH)_2 + 2\,HCl.$$

(*c*) **Salts of Chromium.** — Chromous oxid and hydroxid form salts with many of the acids, but they are so unstable that they are of little importance. The chromic salts are those that will be considered here.

Chromic Chlorid ($CrCl_3$).— Besides the usual method for preparing chlorids, this salt is produced by passing chlorin gas over highly heated chromic oxid mixed with carbon. It is converted into a vapor, and condensed into crystals that are pink to violet in color. The chlorid formed in the wet way crystallizes out of solution with six molecules of water, $CrCl_3.6\,H_2O$. These crystals are green. When the crystalline chlorid is heated, it is decomposed, and a basic chlorid is formed.

$$CrCl_3 + H_2O = CrOCl + 2\,HCl.$$

The sublimed chlorid is very slowly soluble in water, unless there is present a trace of chromous chlorid. It forms double chlorids especially with the alkali chlorids, *e.g.* with sodium. They are $NaCrCl_4$ and Na_2CrCl_5.

Chromic Sulfate ($Cr_2(SO_4)_3$); Crystals ($Cr_2(SO_4)_3.15\,H_2O$).— Chromic sulfate, like other salts of the metal, produces solutions, either violet or green, according to treatment. The crystals produced by dissolving chromic hydroxid in concentrated sulfuric acid, leaving the solution standing in the air, are violet in color and contain $15\,H_2O$. When these crystals are removed and dissolved in water, they can be reformed by adding alcohol to the solution. When they are boiled in water, the solution becomes green; and when evaporated, there is left a greenish amorphous mass, which when dried at 370° becomes an anhydrous insoluble substance, which probably is the normal sulfate ($Cr_2(SO_4)_3$). The green solution becomes reddish violet on standing in the air. What is true of the sulfate in reference to changes of color in its solution is true of the other salt of chromium. An unquestioned explanation of these phenomena has not been made, but it is probably due to the amount of water combined in the normal molecule of the salt. The violet crystals, for example, when heated to 100°, give up water and become green, and the residue contains $5\,H_2O$.

Chromic sulfate forms double sulfates with the alkali sulfates, *i.e.* it forms alums. These salts contain a molecule of each chromic sulfate and one of the alkali sulfates. They crystallize readily from water solutions containing 24 molecules of water, *e.g.* $K_2SO_4.Cr_2(SO_4)_3.24H_2O$. All of this water is driven off at 370°.

These alums produce green solutions when boiled or when heated to 70°, from which crystals cannot be immediately prepared. On standing for a long time, however, the solution changes color, as do the solutions of other salts of chromium, and dark violet crystals are deposited. Chrome alum is used in certain tanning processes and in calico-printing.

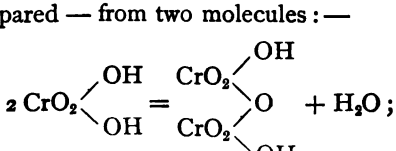
Chromates. — Reference has been made to these compounds in the study of other compounds of chromium. The weak (acid) hydroxid (H_2CrO_4, or $CrO_2(OH)_2$) forms, with the stronger bases, quite stable salts. (Compare with the weaker carbonic acid.) These salts are all highly colored, and are quite generally yellow amorphous powders. They are formed, as we have seen, by the oxidation of the chromic compounds by powerful oxidizers at high temperature in presence of alkaline bases. The normal chromates have the form R_2CrO_4, and are isomorphous with the sulfates. These compounds are powerful oxidizers at ordinary or slightly raised temperatures. They are usually used for this purpose in connection with sulfuric acid, since this acid removes the alkaline base that is necessary to their formation, and also forms, with the reduced chromium, a soluble salt. It is, therefore, the trioxid that is the oxidizer, as was seen under this subject.

Chromium, therefore, from what has been learned in its study, is a strong reducing agent if it is in the chromous condition. Oxidizing agents at moderate temperatures change it to the chromic condition; but if it is in the trioxid form, it is a powerful oxidizing agent, changing it to its most stable form (Cr^{III}). (Compare with iron and manganese.)

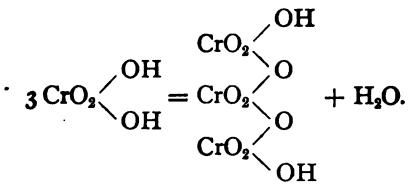
Potassium Dichromate ($K_2Cr_2O_7$). — The dichromates are produced with the stronger bases only. Potassium dichromate is the source of all the compounds of chromium. In the process of manufacture when the calcium chromate is produced, it is purified by grinding up the fused mass, and treating it with water and sulfuric acid. The sulfuric acid unites with the unchanged lime, and also removes a portion of it from the calcium chromate. The reactions are: —

$$CaO + H_2SO_4 = CaSO_4 + H_2O;$$
$$2\,CaCrO_4 + H_2SO_4 = CaCr_2O_7 + CaSO_4 + H_2O.$$

The calcium sulfate is quite insoluble, while the chromate is readily soluble. The sulfate is filtered out, the filtrate concentrated, and there is added to it a solution of potassium sulfate, or, better, one of potassium carbonate. The insoluble calcium carbonate (or sulfate) is formed, leaving in solution the potassium dichromate ($K_2Cr_2O_7$). This compound crystallizes in red plates or prisms, which may be regarded as the normal chromate plus the trioxid ($K_2CrO_4.CrO_3$, or $K_2O.2\,CrO_3$). The dichromate may be considered as the analogue of the pyro-sulfates, and may be regarded as formed by the removal of one molecule of water from two molecules of the hypothetical acid (H_2CrO_4), or as the same acid to which the acid oxid has been added. Higher polymers are often prepared. For example, when the dichromate is acted upon by concentrated nitric acid, more of the potassium is removed, and the poly-chromates are formed. The tri- and tetra-chromates ($K_2O.(CrO_3)_3$ and $K_2O.(CrO_3)_4$) have been prepared. These may be considered as prepared from the hypothetical chromic acid by the removal of water in the same way that the pyro-acids are prepared — from two molecules: —



or, from three molecules: —



The dichromate is a very stable compound, which may be heated to the temperature of fusion without decomposition. Heated above red heat, it is decomposed into K_2CrO_4 and Cr_2O_3 and oxygen: —

$$2\ K_2Cr_2O_4 = 2\ K_2CrO_4 + 3\ O + Cr_2O_3.$$

With sulfuric acid and a reducing agent one molecule always yields three atoms of oxygen. The reduction is expressed thus: —

$$K_2Cr_2O_7 + 4\ H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4\ H_2O + 3\ O.$$

The dichromate is nearly always used with sulfuric acid when used as an oxidizer. Its action towards such reducing agents as hydrogen sulfid and sulfur dioxid has already been examined in the last experimental study. The dichromate is changed to the normal chromate by an alkali; or, on the other hand, a chromate is changed to a dichromate by such acids as sulfuric and nitric acids. Alkali carbonates are decomposed by the dichromates, with the formation of the normal chromate. The dichromate is the source of all the other compounds of the metal. The useful chromium sulfate and its alum are generally waste products of some process in which the dichromate is used.

When the dichromate is dissolved in hydrochloric acid, the compound undergoes a change that explains, in part, the for-

mation of the chromyl chlorid (CrO_2Cl_2). A compound is formed that contains chlorin, having the composition: —

$$CrO_2\begin{matrix}\diagup OK \\ \diagdown Cl\end{matrix}, \text{ or } KCrO_3Cl,$$

called potassium chlor-chromate.

$$K_2Cr_2O_7 + 2\,HCl = 2\,KCrO_3Cl + H_2O.$$

When this compound is treated with potassium hydroxid, the following reaction occurs: —

$$CrO_2\begin{matrix}\diagup OK \\ \diagdown Cl\end{matrix} + KOH = CrO_2\begin{matrix}\diagup OK \\ \diagdown OK\end{matrix} + KCl.$$

This compound, the chlor-chromate, is therefore intermediate between chromyl chlorid and the normal chromate.

Potassium dichromate is used in large quantities for batteries, in dyeing and calico-printing, in photogravure, and as an oxidizing agent in manufacturing and laboratory processes. Several million pounds of the dichromate are used in the United States alone annually.

Potassium Chromate (K_2CrO_4). — Potassium chromate is typical of the alkali chromates. It is a yellow crystalline compound without water of crystallization. It is produced from the dichromate by treating it with an alkali or an alkali carbonate.

$$Na_2CO_3 + Na_2Cr_2O_7 = 2\,Na_2CrO_4 + CO_2.$$

The salt gives an alkaline reaction, and is decomposed by most other acids. It is used as a source of the insoluble chromates.

Lead Chromate ($PbCrO_4$). — Lead chromate, or chrome yellow, is insoluble, and consequently is made by precipitation.

It occurs native, and is known as crocoisite. The artificially prepared chromate is used as a yellow pigment. It is a very

stable compound, and is not decomposed at its temperature of fusion. Like all the chromates, it is a powerful oxidizer, and is often used in ultimate organic analysis for the purpose of oxidizing organic matter. Potassium hydroxid produces a partial decomposition of this compound, forming a basic salt ($(PbOH)_2CrO_4$), called chrome red.

Other Compounds of Chromium. — Chromium forms a compound with fluorin, which is of interest, since it is a volatile compound, and also one in which the chromium is a hexad. The formula for this compound is CrF_6. Like many other fluorids, water decomposes it, forming the trioxid and hydrogen fluorid. It may, therefore, be regarded as the trioxid in which oxygen has been replaced by fluorin. It is produced by the action of calcium fluorid (CaF_2) on lead chromate ($PbCrO_4$) in presence of fuming sulfuric acid. The reaction is: —

$$3\,CaF_2 + 4\,H_2SO_4 + PbCrO_4 = 3\,CaSO_4 + PbSO_4 + CrF_6 + 4\,H_2O.$$

Chromium hexa-fluorid is a very volatile liquid resembling chromyl in its properties.

Soluble chromates form precipitates with most of the soluble salts of the metals, or the chromates are generally quite insoluble. Those of silver (Ag_2CrO_4) and barium ($BaCrO_4$) have been noticed in the experimental study.

ALUMINIUM.

Occurrence and Distribution. — Aluminium, as to quantity, stands third in the list of substances that make up the earth's crust. It is widely distributed in the form of silicates, oxids, hydroxids, and fluorids.

It constitutes a part of the compounds that make up a greater portion of the soil and of the rock masses of the earth. Its

universal distributions in clay make it unnecessary to mention particular localities where the compound may be found. It is never found free.

Preparation. — Aluminium is separated from its native compounds with great difficulty. The oxid is not reduced by the action of carbon under the usual conditions, as is the case with many of the metallic oxids. Owing to the difficulty of separating this metal, it was not prepared until recent times.

It was originally prepared by heating aluminium chlorid with potassium, in closed vessels. Owing to the greater affinity of potassium for the chlorin under these conditions, the aluminium is set free. Until within a few years this process, which has been improved from time to time, was the only one that was used for the preparation of the metal. The chlorid is not found in nature, and consequently must be prepared, and further the cost of sodium (which was substituted for the potassium of the earlier process) of necessity made the cost of the metal relatively great in spite of its abundance. The reaction that occurs readily shows that the price of the metal, by this process, depends largely on the price of the sodium: —

$$3\,Na + AlCl_3 = 3\,NaCl + Al.$$

Suppose, therefore, that the amount of aluminium could be produced in practice exactly in accord with this equation, it is seen that 1 kg. of sodium would produce only .39 kg. of aluminium. The Castner process (see under SODIUM) for the preparation of sodium has cheapened this method of production to such an extent that it is now used quite extensively in the manufacture of aluminium.

The chlorid is generally prepared from a native hydroxid, called bauxite ($Al_2O(OH)_4$), by fusing it in proper furnaces with sodium carbonate, which converts it into sodium aluminate ($Al(ONa)_3$). This is separated from the impurities of the ore by treating the cooled mass with water, which dissolves the

aluminate. Sufficient hydrochloric acid is added to this solution to nearly neutralize it. This action leaves the aluminium as aluminium hydroxid ($Al(OH)_3$). This insoluble compound is mixed with sodium chlorid and carbon, completely dried and heated to a high temperature, in the presence of chlorin. A double chlorid of sodium and aluminium is thus produced, which is a gas at red heat. It is therefore separated by sublimation. The pure chlorid is now mixed with sodium, and the mixture is placed in a furnace and covered with cryolite. The latter substance fuses at a comparatively low temperature and serves as a flux. The sodium sets free the aluminium, which is fused together and collects on the hearth of the furnace.

Within a short period, the manufacture of the aluminium from the oxid has been successfully accomplished. The decomposition of the oxid is accomplished by means of a powerful electric current. Iron crucibles are lined with thick sheets of gas carbon and filled with the oxid (bauxite), with which is mixed sufficient cryolite to constitute a flux. The iron crucible is connected with the negative pole of the electric current. The positive pole consists of several pieces of gas carbon connected together, which are placed in the mixture to be reduced. The intense heat produced by the current fuses the cryolite in which the aluminic oxid floats, and under these conditions it is completely reduced by the carbon of the pole, and the metal gathers at the bottom of the crucible, from whence it is removed from time to time.

The oxygen of the aluminium oxid unites with the carbon of the positive electrode, forming the usual product, carbon dioxid. It is said that a pound of gas carbon produces about one pound of aluminium.

Experimental Study, No. 23. — (*a*) Examine a piece of aluminium for its physical properties. Determine its specific gravity; also melting-point.

(*b*) Heat a piece of the metal in air, and also note the action of H_2S on it.

(*c*) Determine the action of each of the acids on the metal. Describe and write the reactions.

(*d*) Determine the amount of hydrogen that a given weight of aluminium sets free, using hydrochloric acid, according to methods already given. If the amount of hydrogen is considered as unity, to how much aluminium is it equivalent? Evaporate the solution to dryness in which the action occurred. Of what is the residue composed? Heat a little of it in a dry tube to a high temperature. Dissolve residue and test for chlorin and aluminium. (See next study.)

(*e*) Use a solution of sodium hydroxid in place of the hydrochloric acid, and study the result in reference to hydrogen, as in (*d*).

(*f*) Place a piece of aluminium foil in a test-tube, and boil it in water. Note and explain the action. Compare with the action of sodium with water.

(*g*) Melt a few small pieces of lead, and add small pieces of aluminium to the molten mass.

Physical Properties. — The element aluminium is one of the lightest metals, standing seven among the ordinary metals, beginning with lithium, the lightest metal. It is the lightest metal that is not rapidly oxidized in the air. It is lighter than the diamond and heavier than graphite. A cubic centimetre weighs 2.56 g., while the same volume of iron weighs 7.8 g. It weighs, volume for volume, almost exactly the same as marble. It is harder than tin or silver, and nearly as hard as pure iron. It is ductile, and is malleable at temperatures varying from ordinary temperatures up to near the fusion point (best between 100°–200°), becoming harder and more compact by hammering or rolling. It has about the tensile strength of silver. The metal is a good conductor of heat and electricity, standing between copper and silver as a conductor of

electricity, and between zinc and brass as a conductor of heat. It fuses at about 700°, and at this temperature alloys with many of the metals.

Chemical Properties. — One of the most valuable chemical properties of aluminium is its inertness towards oxygen at ordinary temperatures. It is slightly oxidized at temperatures near its fusing-point. At the boiling-point of water, aluminium slowly decomposes it, acting like sodium, except that the action is very slow. It is not dissolved by nitric acid, and is but slowly acted upon by sulfuric acid. Hydrochloric acid readily dissolves it, forming the usual products, hydrogen and the chlorid.

The fixed alkalis, like NaOH, readily dissolve it, hydrogen being set free, and a compound called sodium aluminate is formed. This compound may be regarded as sodium hydroxid, in which the hydrogen is replaced by aluminium. (See ALUMINATES.) Organic acids, such as acetic acid, do not act upon the metal unless there is present some chlorid, especially the alkali chlorids.

Name and History. — The fact that aluminium is never found native, and that it is separated with great difficulty from its compounds, places it in the list of the recently discovered elements. Its preparation was first announced by the celebrated Wöhler in 1828, the year in which he published an account of the artificial preparation of the first organic compound (urea). Aluminium oxid was known to the earlier chemist as a substance prepared from alum, but it was thought that it was lime or a substance closely related to it. In 1754, Marggraff announced that a study of this substance showed that it possessed quite different properties from lime. Later, when Davy applied electricity to the decomposition of compounds, he examined this oxid, but was not able to decompose it. The principle employed by Wöhler, that of the affinity of sodium for chlorin at high temperatures, has been given under preparation 186.

The method of preparation was not much improved until 1854, when Deville improved the process, and the metal was prepared commercially, although the cost was such that it could not be employed for general purposes. Since then the aim has been to cheapen the process, and generally by lowering the price of sodium. These improvements, taken in connection with the application of electricity to its separation, have reduced the price of the metal from about twenty dollars to less than seventy-five cents per pound, at which price it will probably remain unless lowered by competition.

The name is derived from alum (or alumen). The word refers to the astringent property of the substance.

Atomic Mass and Valence. — Berzelius was the first to determine the equivalent of aluminium. His determination made the number 27.3. The next reliable work was done by Mallet about 1880. Mallet used several methods, among which were those of the hydrogen set free by pure aluminium acting on potassium hydroxid, and those of the equivalence of silver and aluminium. He found that with silver as 107.7, aluminium is 27.11. Pure aluminium bromid was prepared, and this solution was treated with a solution of silver nitrate so made that the amount of silver in each cubic centimetre was known, and therefore the amount of silver that was exchanged for the aluminium became known. The reaction is: —

$$AlBr_3 + 3\,AgNO_3 = 3\,AgBr + Al(NO_3)_3.$$

The hydrogen evolved by a given mass of pure aluminium was oxidized and the water weighed, and the calculations made on the basis of two atoms of aluminium to each three molecules of water that were formed. (See last study (*d*) and (*e*) for hydrogen equivalent of the metal.)

Aluminium forms several compounds that are gaseous, among which are several organic compounds and the chlorid and bromid. The vapor density of the chlorid and bromid has

been determined to be 133.15 and 266.31, or the molecular masses are 266.3 and 532.62, respectively.

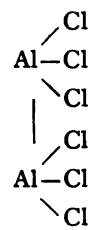
According to the results of quantitative analysis, these molecules contain 54.08 parts of aluminium united with 212.22 parts of chlorin or with 478.56 parts of bromin.

Recent study of these compounds shows that the vapor density of these compounds decreases until a high temperature is reached, when it becomes constant. For example, the chlorid boils at 180°, and when this vapor is heated, its density gradually decreases until a temperature of about 800° is reached. At this point its vapor density is 66.57. It was found that up to 1500° this density was constant. The number 66.57 corresponds to a molecule having 27.04 parts of aluminium and 106.11 parts of chlorin. It is evident, therefore, that there are two gaseous molecules of the chlorid, one of which contains just twice as much of aluminium and chlorin as does the other. The organic compounds contain 27.04 parts of aluminium, and this is the smallest amount found in any of these molecules; *i.e.* this is the amount of the element according to molecular mass as determined by vapor density, when carbon is 12 and hydrogen is one.

It is evident from these facts that the molecule of the chlorid is decomposed by heat into two molecules, and so far as has been observed, that these new molecules are not further decomposed without dissociation of the elements. The atomic mass, therefore, is 27.04. This number agrees with that formed from the specific heat. But 27.04 parts of aluminium are combined with 106.11 parts or 3 atoms of chlorin (or bromin). The formula for the chlorid is then $AlCl_3$ or Al_2Cl_6. Both represent the facts of percentage composition; the first is the simpler and is used in this text.

From the facts just given, aluminium is a triad, or what is sometimes called a "pseudo-triad." The compound is explained on this basis by saying that two groups ($AlCl_3$) are

held together by a fourth unit of valence. The compound is represented thus: —



It is quite probable that many molecules of the same kind unite in a similar manner. This is probable, as has been seen in case of the ferric chlorid, sulfur, etc. Heat may destroy all valence or may decrease it. For example, chromium is a hexad or triad according to the temperature to which its compounds are exposed. When an element has united with all it can of a given element at ordinary temperatures, there may remain sufficient holding power to fix other like or even different molecules. Double salts have already furnished examples of this action.

Aluminium chlorid forms several characteristic double salts. There are no binary compounds known in which aluminium acts as a tetrad. This would be expected to be true if it is not a true triad. Polymerization finds its explanation in the incomplete saturation of valence of one element by different elements. In many cases the residual of valence, so to speak, is scarcely sufficient to hold another molecule, while in others the residue is such that the double molecules nearly always exist at ordinary temperatures. Examples illustrating these statements are quite common in organic chemistry. Examples that have been seen already are arsenious oxid, —

As_2O_3(or As_4O_6), $SnCl_2$ (or Sn_2Cl_4), Sb_2O_3 (or Sb_4O_6), etc.

Aluminium is a triad in all of its compounds.

Uses. — Probably no element has been more often written about from the standpoint of usefulness than has aluminium. The cost of preparation has until recently prevented its use on an extended scale. Its low specific gravity, its beauty when polished, and its resistance to the action of the atmospheric agents have suggested many uses for the element. It is used for the beams of balances, many kinds of scientific apparatus, and for making ornamental objects. The greater portion of the metal that is a commercial article is used alloyed with copper. This alloy, called aluminium bronze, contains about ten per cent of aluminium and ninety per cent of copper. This substance quite resembles gold in color, is quite hard, and is nearly as resistant to corrosion as is aluminium. It expands measurably on cooling from fusion, and is consequently used in casting; it is tough and malleable, and quite perfectly homogeneous.

Aluminium and iron alloy, and a small amount of the former metal, impart a very valuable property to steel; namely, it enables the manufacturer to produce a very homogeneous steel casting. It is claimed that the very small amount of aluminium present improves the general quality of the steel. A large amount of aluminium is now used for preparing the "Mitis casting." About one-tenth of one per cent of aluminium is added to the iron.

Experimental Study, No. 24. — (Material: a solution of the salt made in the last study or one of any of the soluble salts of aluminium and the usual reagents.)

(*a*) Study the solubility of the various compounds, noting effect of excess of reagents, heat on the same, etc. Write all reactions. Place results in table of solubility. H_2S has no action on salts of aluminium. $(NH_4)_2S$ and soluble carbonates precipitate $Al(OH)_3$. (Note particularly the appearance of the hydroxid.) Study the effect of NH_4Cl on the solubility of the hydroxid produced by the fixed alkali hydroxid. Add

an excess of the chlorid. $K_4Fe(CN)_6$, $Na_2S_2O_3$, $Na_2B_4O_7$, all produce hydroxids with soluble salts of aluminium.

(*b*) To a solution of the salt of aluminium add KOH slowly, and boil. The compound is $Al(OK)_3$. Next add ammonium carbonate and ammonium hydroxid to portions of the solution. Carefully neutralize the excess of alkali with HCl. Explain.

(*c*) Filter out the aluminium hydroxid and dry it. Transfer a portion to charcoal or to a piece of platinum foil and heat to bright redness. Now moisten with a solution of cobalt nitrate and reheat to highest temperature. Note the color of the mass. This is a characteristic test for aluminium. The cobalt is decomposed, leaving cobalt oxid (Co_2O_3), which forms the colored compound with the aluminium oxid (Al_2O_3). Or heat strongly in the oxidizing flame a little alum on platinum wire in the same manner as for making a borax bead. Moisten in the cobalt solution and heat strongly again.

(*d*) Heat strongly a crystal of aluminium sulfate on charcoal. Remove the residue and boil in water. Filter, and test for sulfuric acid. Where is it? Heat some of the same salt in a test-tube. What escapes? Prove it. What is left, judging from what is set free?

Dissolve some of the sulfate, and test it with litmus. What inference can you draw as to the basic character of aluminium? Compare with its action on carbonates. Also its action towards strong bases like KOH, already studied. Heat some of the hydroxid formed in (*a*) or (*b*) with sodium carbonate, using an excess of the hydroxid. What gas escapes? Test the residue with a drop of acid. Explain the result.

(*e*) To about 15 g. of clay add 4 to 5 cc. of sulfuric acid, stir together, and heat on water-bath for an hour or more. Cool, and add water, stirring the mass well, and then boil and filter. Clay after drying is aluminium silicate ($HAlSiO_4$) (see under CLAY). Write the reaction, and account for the residue and the substance in solution. Evaporate off nearly all of the

water and allow the solution to cool. Remove the solid and add just water enough to redissolve it. Add a saturated solution of potassium sulfate. Heat, if a precipitate is formed on mixing the two solution. Cool, and note the crystals. They are $K_2SO_4.Al_2(SO_4)_3.24\,H_2O$ or $HAl(SO_4)_2.12\,H_2O$.

(*f*) Grind to a very fine powder pure sand (like sea-sand), and add to it about three times its bulk of sodium carbonate, and place in a small crucible and heat to quiet fusion. While it is hot, touch it with a glass rod, and withdraw the rod. Compare its general appearance with glass. Note the escaping gas. What is it? The compound is sodium silicate (Na_2SiO_3). Write the reaction.

(*g*) Grind up a few cochineal insects, and boil in water for a few minutes. Filter, and to the solution add a solution of alum. Stir well, and add NH_4OH to complete precipitation. Shake well and filter. Where is the coloring-matter? If any coloring-matter remains, add more of the alum solution, and follow it with NH_4OH.

(*h*) Prepare a solution of cochineal, or one of logwood, by dissolving the solid extract. Cut strips of cotton cloth, and dip one of the strips in a solution of alum, and then in a dilute solution of ammonia. Without drying, dip this strip in the coloring solution. Prepare another strip in the same way, except that it is not dipped in the alum solution. Boil the cloth in the colored solution for five to ten minutes. Cool, and wash the pieces in water, and dry them. Explain these results in the light of (*g*).

(*i*) Dissolve a few grammes of aluminium sulfate in water, and test it with litmus paper. To a portion of the solution add a piece of zinc. What gas escapes? Prepare some aluminium hydroxid, and add it to some of the original solution. Warm basic salts are produced of variable composition. The formulæ $Al_2O_3.SO_3$, $Al_2O_3(SO_3)_2.H_2O$ represent two such products. Write the reaction in both cases.

Compounds of Aluminium.

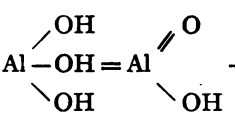
(*a*) **Oxid.** — Aluminium, as has been shown, is always a triad, and hence forms but one oxid, Al_2O_3. It is soluble in acids when produced from the hydroxid, if it has not been too strongly ignited. When it has been strongly heated, it is insoluble in all acids. It is infusible, excepting at the highest producible temperatures. It fuses in the oxy-hydrogen flame. When the fused mass cools, small crystals are formed which resemble the native corundum. When fused with alkali hydroxid, or with the acid sulfate of potassium, it forms soluble compounds.

Aluminium oxid, or alumina, is found in nature very nearly pure in such minerals as the ruby, sapphire, corundum, and emery. These minerals are in the form of crystals, or in crystalline masses. They are very hard, the sapphire standing nine in the scale of hardness. (The diamond, the hardest substance, is ten in the same scale.) The great beauty and hardness of these minerals make them very valuable for ornamental purposes. The ruby, as its name indicates, is a brilliant red crystal of the nearly pure oxid, the coloring-matter, chromium oxid, being the only impurity. The ruby is produced artificially by heating together barium fluorid and alumina, or a mixture of aluminium fluorid and boron trioxid. By adding potassium dichromate, or a cobalt compound, to the mixture, the crystallized oxid is colored ruby red or sapphire blue. Artificial rubies and sapphires are produced in this manner that are said to equal, if not to excel, in beauty the natural gem. When the oxid is ignited with cobalt oxid, a blue compound is produced, which is characteristic, and serves to distinguish aluminium oxid from many other substances which resemble it in general appearance. Owing to its hardness, emery is used for grinding and polishing hard substances, such as glass, iron, and steel. Aluminium oxid acts

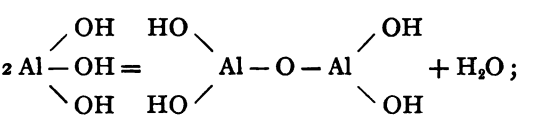
both as a weak base and a weak acid, forming salts and compounds called aluminates (which see).

(*b*) **The Hydroxid.** — Aluminium hydroxid ($Al(OH)_3$) is a gelatinous, translucent substance when produced in the wet way, which becomes a yellowish horn-like mass when dried. It is, like the oxid, a weak base, but in connection with strong bases it acts like a weak acid. It is found in nature, and is known as hydrargylite.

Aluminium hydroxid, like the corresponding one of iron and many other bases, loses water gradually at ordinary and at higher temperatures with a condensation of the molecules. From one molecule of the hydroxid a molecule of water escapes when carefully heated to 300°, forming a compound corresponding to ferric meta-hydroxid ($FeO-OH$) and chromium meta-hydroxid ($CrO-OH$).



This aluminium meta-hydroxid occurs in nature as the mineral diaspor corresponding to pyro-siderite (ferric meta-hydroxid). Again, two molecules of the hydroxid are decomposed, thus: —



i.e. two groups, $Al(OH)_2$, are joined by an atom of oxygen which is derived from two molecules of hydroxyl. This basic hydroxid is found in nature in the mineral bauxite. This mineral received its name from the town of Baux in France, where it was first found. It contains, in addition to alumina, iron, oxid, and silica.

The meta-hydroxid (AlO.OH), under certain conditions, acts as an acid; *i.e.* its hydrogen can be replaced by a metal. This hydroxid, and the corresponding ones of iron and chromium, form a class of native compounds called spinels. These compounds are illustrated by crysoberyl, $\begin{matrix} O=Al-O \\ O=Al-O \end{matrix}\!\!\searrow\!\!\swarrow Be$; magnesium aluminate, $Mg(AlO_2)_2$; franklinite, $\begin{matrix} O=F-O \\ O=F-O \end{matrix}\!\!\searrow\!\!\swarrow Zn$; magnetite, $\begin{matrix} O=Fe-O \\ O=Fe-O \end{matrix}\!\!\searrow\!\!\swarrow Fe$; chrome iron, $\begin{matrix} O=Cr-O \\ O=Cr-O \end{matrix}\!\!\searrow\!\!\swarrow Fe$. Compounds with other bases are well known. When the compounds are produced by heat in the dry way, they are very stable. The native compounds are very stable, while the corresponding alkali compounds produced in the wet way are quite unstable. Those of iron and chromium are decomposed by boiling. The fixed alkali aluminate is not decomposed by boiling in an excess of the alkali, and this serves to separate aluminium from iron and chromium when they are mixed and combined as hydroxids. The reaction is: —

$$Al(OH)_3 + 3\,NaOH = Al(ONa)_3 + 3\,H_2O.$$

Aluminium hydroxid in the moist state has the property of uniting with certain organic coloring-matters, forming with them very stable compounds called "lakes." Many of the colored compounds are made, and then dried and ground up to serve as pigments in painting. Also when this lake is formed in contact with cotton and other vegetable fibre, it adheres so firmly to it that ordinary washing does not remove it. Such a color is said to be "fast." Aluminium hydroxid (and other substances that produce this result) are called mordants, which literally refers to the "biting" or holding of the color. Sodium aluminate is used as a mordant. Large quantities of it are prepared by

fusing together either diaspor or bauxite with sodium hydroxid, or by fusing a mixture of cryolite and calcium oxid (lime). In any case the product is sodium aluminate.

$$AlO.OH + 3\ NaOH = Al(ONa)_3 + 2\ H_2O;$$
$$Al_2O(OH)_4 + 6\ NaOH = 2\ Al(ONa)_3 + 5\ H_2O.$$

When cryolite is fused, the following reaction occurs: —

$$Na_3AlF_6 + 3\ CaO = Al(ONa)_3 + 3\ CaF_2.$$

The sodium aluminate is soluble in water, and is thus readily separated from the insoluble calcium fluorid. These alkali aluminates, when used for mordants, are decomposed by treating their solution with carbon dioxid, which decomposes them, forming sodium carbonate and aluminium hydroxid. The aluminates are decomposed by any acid forming the corresponding salt of aluminium and the base of the aluminate.

The hydroxid is used as a clarifying agent in case of sugar solutions and other liquids holding matter in suspension. The precipitate hydroxid forms a gelatinous mass which settles, carrying down the suspended matter.

(*c*) **Salts.** — Aluminium is a weak base, and its principal salts are formed with the stronger acids. It does not form carbonates or sulfids in the wet way. The chlorid has been sufficiently described under the study of the atomic mass of the element.

Silicates. — Aluminium, as we have seen, is widely distributed in nature in combination with silica, and constitutes large rock masses. These compounds are complex, and are variously constituted. They are known as feldspar, mica, clay, kaolin, and a great variety of less important minerals. These minerals are not pure aluminium silicate, but are combinations of this silicate with one or more other silicates. The most important of these compounds are the double silicate of aluminium and one of the alkali metals. In Part I., pages 333 and 334, attention was

called to the tendency of silicic acid to form poly-acids and salts. It was noticed that several of these acids are recognized; *i.e.* there are salts found in nature corresponding to several of these poly-acids. Aluminium enters into a large number of these poly-silicates, but it would take us too far from the object of this work to enter into a discussion of the composition of these complex compounds. They are such very insoluble substances, and so few reagents act upon them, that they are not yet fully understood. The most important and abundant of the silicates are the feldspars, orthoclase, and albite. They are the potassium and sodium aluminium tri-silicates ($KAlSi_3O_8$ and $NaAlSi_3O_8(H_4Si_3O_8)$). There are other feldspars in which calcium replaces the alkali bases. They always contain aluminium oxid and silica with one or more other stronger bases. Another silicate, known as leucite, is a meta-silicate, and has the composition represented by $AlK(SiO_3)_2$. The two feldspars mentioned form a large part of the rock masses of the earth that are of igneous origin.

Clay: its Origin.—When the different feldspars come in contact with natural waters and the air, they are slowly decomposed. As has been seen, the alkali silicates are soluble in water, and under the influence of the natural water, which contains carbon dioxid, organic and inorganic acids, the feeble union between the two silicates is destroyed, and the aluminium silicate (insoluble) and the potassium or sodium silicates are separated. The alkali silicates are in turn decomposed by acids (and other soil substances), the alkali salt being washed away, or it may be taken up by plants. The aluminium silicate takes up water in varying amounts, forming hydrated silicates. Some of the common forms are represented by $Al_2H_2(SiO_4)_2.H_2O$ and $Al_4(SiO_4)_3.4\,H_2O$.

It is readily seen that a mass of pure feldspar disintegrating as just described would leave a residue of pure hydrated aluminium silicate. Such a pure clay is called kaolin. Again, if

a granite is decomposed, its insoluble quartz and mica are left mixed with the kaolin, and form a larger or smaller part of the whole residue, depending on the kind of granite from which it is produced.

The two cases of decomposition of feldspar mentioned suppose that all but the insoluble products remain in their original position. This is undoubtedly true in some cases; but quite generally the insoluble parts of the decomposition are carried by water currents and deposited in various positions along the course of the flowing water. The particles of kaolin are very small, having been produced by chemical disintegration, while the quartz and mica, which are mechanically formed, are left in much larger particles. The minute particles of kaolin are held in suspension longer in still water than are the coarser particles referred to, and consequently are more or less perfectly separated into an upper layer when settling from water holding in suspension both kind of particles. (It is probable that water has an adhesive action towards kaolin particles, and that they are held in suspension longer than the same sized particles of silica, although the specific gravity is about the same number for both.) The effect of this is, when the water is running, to separate the kaolin from the usual impurities, and to deposit it in the form of fine mud in the quiet water. But usually some of the decomposition products are deposited with it, or other impurities are carried to the same place, so that the general result is that an impure kaolin or a clay is formed. Iron compound and calcium and magnesium carbonates are common impurities.

Kaolin. — The purest clay is called kaolin, and in this condition is nearly pure white in color. This substance is practically infusible, but when well moistened with water and worked, the mass becomes plastic, and can be made into a variety of forms. When the moulded kaolin is dried, it forms an adherent, but quite porous, mass like sun-dried bricks, but when heated

to a high temperature called "burning," the mass becomes hard and compact. Somewhat impure kaolin is used in this manner for "fire-bricks." The impurity must be, however, some substance that does not fuse. Usually much sand is mixed with the clay.

In the manufacture of the finest kinds of earthenware from kaolin, there is mixed with it a little pure feldspar and sand. The finely powdered mixture is moulded into the form desired, and dried at low red heat. It is then heated to a temperature sufficiently high to fuse the feldspar (about white heat), which forms a glassy mass that is quite translucent. Fluorspar takes the place of the feldspar in many cases. Such earthenware is called "china" or porcelain. If the kaolin alone is used, the article shrinks and cracks, and warps out of shape. The sand prevents this cracking, and makes the mass more compact. The porcelain is glazed by some of the processes given for glazing the more common earthenware, except that the purest materials are used.

The more impure forms of kaolin are used for the ordinary earthenware. It is thoroughly stirred in water, and many of the coarser impurities, which settle out at first, are removed. The finer residue is mixed with feldspar and sand (if necessary), and moulded into the shapes desired. It is then heated for some time to a high temperature, but not sufficiently high to fuse the mixture. The surface of the article is glazed by covering its surface with such fusible mixtures as sand, aluminium oxid and sodium carbonate, or lead and tin oxids, mixed with sand, or lead oxid and borax. These glazes are very finely divided, and mixed with water, and spread carefully over the surfaces to be glazed. Chinaware is given a richly glazed surface by covering its surface with very finely powdered pure feldspar when it is heated to a temperature of fusion.

Clay, for the manufacture of the finer kinds of earthenware, must be free from iron hydroxid, one of its common impurities,

since it imparts to it, when heated (baked), a yellowish red to a bright red color. The impure clays are used in the manufacture of coarser earthenware, bricks, tiles, etc. The coarser ware, like "stone jars," is made in very much the same manner as that described for the better article. The glazing is commonly produced by throwing common salt on the vessels while they are being heated in the furnace. The salt is decomposed at the high temperature of the furnace, and the sodium unites with the silicon dioxid and aluminium silicate to form the double salt of sodium and aluminium silicate. This forms a glassy covering over the surface of the article which is impervious to water.

Bricks are manufactured by grinding up the poorer sorts of clay and moulding it into bricks, and heating them to a high temperature for several hours. Bricks vary in color from light straw to a deep red color. This difference in color is due to the amount of the hydroxid of iron present in the clay. The hydroxid becomes ferric oxid under the conditions that obtain in the kiln. If the clay contains several per cent of calcium carbonate, fixed alkali compounds, or iron compounds, the brick is likely to fuse when "baked." The hardness of brick, everything else being equal, depends on the fineness of the material used and the pressure used in forming them.

Aluminium Sulfate ($Al_2(SO_4)_3$); Crystals ($Al_2(SO_4)_3.16H_2O$).—Aluminium sulfate is the source of most of the compounds of this metal. Clay is decomposed by hot concentrated sulfuric acid, forming aluminium sulfate, setting free silica and the impurities of the clay, most of which are insoluble in the acid. The aluminium salt is soluble in water, and when the solution is evaporated, crystals are formed containing 16 or 18 molecules of water, depending on the presence of impurities. The pure salt crystallizes with 16 molecules of water, which are completely driven off at 350°. Red heat decomposes the salt. At low temperatures 27 molecules of water are taken up in crystalliza-

tion. If the clay contains iron, it is precipitated as prussian blue (the iron being in the ferric condition). The solution is evaporated, and the somewhat impure aluminium sulfate is used as a mordant, clarifier, etc. Alum cake is a still impurer form of the sulfate produced by decomposing clay with sulfuric acid and evaporating off the excess of acid. This alum cake is used as a sizing for paper.

Alums. — Salts formed from weak bases and active acids act somewhat like unsaturated compounds. As has been seen, aluminium sulfate dissolves aluminium hydroxid. Now when these salts are brought in contact by solution with the salts of stronger bases, compounds are formed which are very nearly neutral. Several of these double salts have already been studied. Aluminium sulfate forms double sulfates with the sulfates of potassium, sodium, or ammonium. They are called alums, and have several properties in common. They contain the molecular proportions of the two compounds, and when crystallized contain 24 molecules of water. When potassium alum is heated to about 100°, it melts, in its water of crystallization, and if the temperature is kept at 100°, the water is slowly driven off, leaving a white powder called "burnt alum." The last portion of the water escapes at 300°. The ammonium alum is decomposed at high temperatures, leaving aluminium oxid. The latter alum is often used in place of the potassium or commom alum.

Alums are used in large quantities as the source of aluminium hydroxid, which is used as described under hydroxid.

The term *alum* is now applied to a large number of double sulfates in which iron (-ous and -ic), chromium, or manganese has taken the place of the aluminium. The alkali sulfates are those just mentioned, and, in addition, those of lithium, cæsium, rubidium, silver, and thallium. These compounds are perfectly isomorphous. A crystal of common alum grows perfectly if placed in a solution of any one of the other alums. They are

represented by the general formula $M^{I}_{2}M^{III}_{2}(SO_4)_4.24\,H_2O$. The alum crystallizes in octahedral forms.

Aluminium Sulfid. — Aluminium sulfid is not formed in the wet way. The soluble sulfids produce the hydroxid when acting on a soluble aluminium compound. When aluminium is mixed with sulfur and the mixture heated to red heat, the two elements unite to form the sulfid (Al_2S_3). This compound is decomposed by water, producing the hydroxid and hydrogen sulfid in the same manner as are the sulfids of chlorin and phosphorus and those of the other non-metals.

$$P_2S_5 + 8\,H_2O = 2\left(O=P\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix}\right) + 5\,H_2S;$$

$$Al_2S_3 + 6\,H_2O = 2\left(Al\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix}\right) + 3\,H_2S.$$

Separation and Recognition of Iron, Aluminium, and Chromium.

Experimental Study, No. 25. — Mixtures of the soluble salts of aluminium, iron, and chromium (for example, the sulphates) should be prepared and studied for the purpose of separating and recognizing these bases, according to the facts learned in the studies of these elements and their compounds. The mixtures may contain salts of all of these elements or only two of them.

Suppose the mixture contains the three salts, the iron being in the ferric condition, what is the effect of treating the solution with ammonium hydroxid and warming it? Suppose the precipitate is filtered out and boiled with a solution of a fixed alkali hydroxid, what reaction occurs? Write the reac-

tions. What is the residue? Treat a portion with HCl, and add to portions of the solution the reagents KCNS and $K_4Fe(CN)_6$. Fuse the other portion of the precipitate on platinum foil with potassium nitrate and potassium (or sodium) carbonate. Dissolve the mass from the platinum foil and acidify with acetic acid, and test the solution for chromium. (See under CHROMIUM.)

Prove the presence of aluminium in the filtrate from the alkali solution. (See under ALUMINIUM.)

Suppose that the iron present is in the ferrous condition, why must the solution be treated with nitric acid before precipitating with NH_4OH? Suppose that no iron is present in such a solution, is the nitric acid treatment necessary? Why?

Suppose the mixture of the three salts had been treated with $(NH_4)_2S$, in what combinations are the metals after the reaction? Would the treatment with nitric acid be necessary here if all of the metals are to be precipitated? Why? Explain fully.

Suppose that the chromium is in the form of a chromate, how can it be separated and recognized? What is the effect of treating a solution of a chromate with H_2S in the acid solution? Treat a solution of a chromate with H_2S under these conditions. Pass the gas for some time, and then boil the solution until the H_2S has been driven off. Filter out the sulfur and treat with an excess of NH_4OH. Would the chromium have been precipitated by NH_4OH, if it had not been reduced by H_2S?

MANGANESE.

Occurrence and Distribution. — Manganese occurs in nature in combination and is widely distributed. It is often found associated with iron compounds. Plants absorb its compounds from the soil in small quantities, as shown by the fact that

plant ashes nearly always contain small quantities of manganese compounds. The principal native compounds are the oxids and hydroxids, Mn_2O_3, MnO_2, Mn_3O_4, and $MnO-OH$, and named in the order given, braunite, pyrolusite, hausmannite, and manganite. Of these, only pyrolusite and manganite are used as ores.

Preparation. — The ores of manganese being the oxids, the problem is to remove the oxygen from them. When the higher oxids are heated to red heat, they are reduced to manganous oxid (MnO), but this last atom of oxygen is removed with considerable difficulty, resembling aluminium in this respect. Carbon at intense white heat reduces the oxid, however, if it is intimately mixed with it. The oxid is mixed with sugar or oil, and slowly heated to decompose the carbonaceous matter, and finally the whole mass is heated to white heat. The metal can be obtained from the chlorid by fusing it with sodium, when an action takes place similar to that which occurs in preparing aluminium from its chlorid.

Physical Properties. — Manganese is a hard, grayish white metal, resembling iron in its general appearance. It is heavier than iron (specific gravity = 8), crystalline in structure, and, therefore, quite brittle. The metal alloys with carbon and with many of the metals. One of the principal alloys is with iron, which is known under the name of ferro-manganese spoken of under steel manufacture. The pure metal fuses at a high temperature, which is approximately 3000°.

Chemical Properties. — As has been stated, manganese has a great affinity for oxygen. It cannot, therefore, be kept in the air, but must be placed in some gas like nitrogen or hydrogen, or in some liquid that contains no oxygen, like petroleum. It slowly decomposes water at ordinary temperatures, increasing in rapidity as the temperature rises. The products are the usual ones; namely, the oxid and free hydrogen. It forms soluble salts with the principal acids.

Name and History. — The metal was first prepared by Gahn in 1774, although Scheele and Bergmann were the first to recognize that the native braunstein contained a new metal. Braunstein (or Mn_2O_3) was also known as black magnesia, or magnesia nigra. This name was used to distinguish it from white magnesia, or magnesium alba. (The ending *a* was formerly applied to the name of the metal in place of *um* or *ium* to distinguish it from its oxid.) The metal was not separated from the magnesia alba until 1808, and since the metal produced from magnesia nigra had also been called magnesium, a name had to be found for the newly discovered metal. It was finally decided to change the name of what was then magnesium to manganesium or manganese, and to use the name *magnesium* for the metal obtained from magnesium alba.

Atomic Mass and Valence. — Manganese is one of the elements that form no known volatile compound, and hence its atomic mass has not been fixed by a study of such compounds. The first study of its compounds for the purpose of determining this number was made in 1857. This was done by producing manganese sulfid from manganese sulfate. When sulfur is 31.98 and oxygen is 15.96, the amount of manganese in these compounds is 54.8. The specific heat of the element is .1217. This, according to the law of Dulong and Petit, gives an atomic mass nearly coincident with 54.8. This number is, therefore, taken as the atomic mass of the metal.

The element forms but one stable chlorid, in which 54.8 parts of it are combined with 70.74 parts of chlorin. There is formed at least one other chlorid, but it is easily decomposed. From the analogy between manganese and iron and chromium, this compound is thought to be represented by the formula $MnCl_3$ or Mn_2Cl_6. The element is then divalent and trivalent or pseudo-trivalent. A study of the other compounds of manganese indicates that its valence varies from 2 to 7. (See under COMPOUNDS.)

Uses. — The pure metal manganese has not been applied as yet to any useful purpose. Alloyed in small quantities with iron it imparts to it properties that make it very useful. It also serves to remove impurities from the iron during the process of its manufacture. An alloy with iron containing 25 per cent or more of manganese is known as ferro-manganese, and is used in the manufacture of Bessemer steel.

Experimental Study, No. 26. — (*a*) To 5 g. of manganese dioxid add about 30 cc. of concentrated hydrochloric acid, and warm. What gas escapes? Where have you used this reaction before? Heat under a hood or pass the gas into a solution of KOH. Boil until the action is complete, adding more acid if necessary. Evaporate the solution to dryness, and redissolve the residue in water, filtering if the solution is not clear. Where is the manganese? Test the solution for chlorin. Explain in reference to the source of both the free and combined chlorin. With what is the manganese now combined? What has become of the oxygen that was combined with the manganese?

(*b*) Treat another portion of manganese dioxid with concentrated H_2SO_4 in a test-tube. What gas escapes? Treat 5 g. of the dioxid in an evaporating-dish with H_2SO_4. Heat, adding more oxid as long as it continues to be dissolved. Cool, and add a small amount of water, filtering out any unchanged oxid. Allow the solution to cool and evaporate at ordinary temperatures. What is the compound, manganese being divalent? Why is oxygen given off in this case and not in (*a*)? Write the reaction. Suppose the oxid to have been the monoxid, how do the products differ?

(*c*) Using the solutions of the salts just prepared, study the action of the usual reagents on them, writing the reactions. Note the action of NH_4OH, by itself, and also in the presence of NH_4Cl. Note the action of the air on the precipitates, especially on the carbonate and hydroxid. The hydroxid

takes oxygen and forms a compound having the formula $Mn_2O_2(OH)_2$.

(*d*) Place about 5 g. of manganese in an ignition tube and heat to red heat. Test the escaping gas with the red-hot coal. Note and examine the residue physically. It is tri-manganese tetroxid (Mn_3O_4). Write the reaction.

(*e*) Fuse in a test-tube (or porcelain crucible) 4 g. of NaOH and 3 g. of $KClO_3$, and while fused add slowly about 5 g. of MnO_2. When the tube is cool, break it, and to a small portion of the mass add water (filter if necessary), and test for HCl. What does this result show in reference to the changes in $KClO_3$? The green mass is potassium manganate (K_2MnO_4 or $K_3O.MnO_3$). Compare with MnO and MnO_2 as to amount of oxygen. What is the source of the oxygen? How much has been taken up? Write the reaction, applying the rules for balancing such equations given in Part I., pages 272, 273.

(*f*) Fuse on platinum foil a mixture of 2 parts of KNO_3 and 1 part of K_2CO_3 with a small amount of the $Mn(OH)_2$ produced in (*b*). Compare with (*e*). What is the use of the two reagents? (KNO_3 acts like HNO_3 at high temperatures.) Write the reaction. Two molecules of KNO_3 will yield how much oxygen?

(*g*) To the remainder of the fused mass of (*e*) add water, and through a portion of the clear solution pass CO_2. What is the action between KOH and CO_2? Note the changes of color. The compound formed is potassium permanganate ($KMnO_4$). The reaction may be represented thus: —

$$3\,K_2MnO_4 + 2\,H_2O = 2\,KMnO_4 + MnO_2 + 4\,KOH;$$
$$3\,K_2MnO_4 + 2\,CO_2 = 2\,KMnO_4 + MnO_2 + 2\,K_2CO_3.$$

To another portion of the solution add dilute H_2SO_4. What becomes of KOH in this case?

(*h*) To a solution of a ferrous salt, *e.g.* $FeSO_4(FeO.SO_3)$, acidified with H_2SO_4, add slowly a solution of potassium per-

manganate as long as the color of the solution is destroyed. (If a precipitate is formed, add more H_2SO_4.) Determine whether the iron is ferrous or ferric. (See under IRON.) If the iron has been changed, how is the corresponding oxid written? Write the corresponding salt. What is the use of the H_2SO_4? Add NH_4Cl to the solution in excess and remove the iron according to the study given under IRON. To the solution free from iron, add KOH, and determine in what condition the manganese is; *i.e.* what is its valence? How many units of valence has it lost? The iron has gained how many units of valence? How much oxygen has each atom of the iron gained? How much has each atom of the manganese lost? How was the manganese combined after the reaction on the iron salt? (Note the presence of H_2SO_4.) Write the reaction in light of the facts discovered.

(*i*) Pass SO_2 into a warm solution of $KMnO_4$ until the color is destroyed. Boil the solution until all the free SO_2 is driven off. Test the solution for H_2SO_4. Test for free acid. How will the potassium and manganese be combined? Write the reactions.

Compounds of Manganese.

(*a*) **The Oxids.** — Manganese forms several oxids. The possibilities of valence indicate such oxids as MnO, MnO_2, MnO_3. There are, in addition, oxids represented by the formulæ Mn_2O_3, Mn_3O_4, and Mn_2O_7.

Manganous oxid can be prepared in the usual manner, — namely, from the hydroxid, carbonate, or nitrate, — but the decomposition must be done in some inert gas like nitrogen or hydrogen. Any of the higher oxids are reduced to this form by heating in hydrogen. When the oxid is heated in the air (or in some oxidizing substance) in the presence of alkalis, it is readily oxidized to compounds corresponding to the higher

oxids. It is an amorphous green substance which is readily dissolved in acids, forming salts in which manganese is divalent.

Dimanganese trioxid (Mn_2O_3), corresponding to diferric trioxid (Fe_2O_3), is feebly basic, and forms unstable salts with the stronger acids. In acid solution, these salts are changed readily into the manganous salts. The mineral braunite is the native trioxid.

Manganese dioxid (MnO_2) is found in nature in large quantities, and is quite widely distributed. It is commercially known as the black oxid of manganese and as pyrolusite. A hydrated form is called wad. Manganese dioxid is feebly acid, and when heated with strong bases away from the air forms alkali manganite. For example, it is probable that when the dioxid is heated with potassium hydroxid, the reaction is—

$$2\,KOH + MnO_2 = K_2MnO_3 + H_2O.$$

In the air, the potassium manganite (K_2MnO_3) takes up an atom of oxygen and becomes the manganate (K_2MnO_4). This reaction resembles that of the formation of a sulfate from a sulfite when a solution of the latter is exposed to the air.

The dioxid has many applications in the arts, among which are its use in preparing chlorin, as a source of oxygen, in glass-making, and as an oxidizer. It gets its name, pyrolusite (meaning *fire* and *to wash*), from its use in destroying the color in glass, especially that due to iron compounds which make the glass green. When a small amount of the dioxid is fused with the glass, it oxidizes the iron compounds to colorless or slightly colored ones, and the manganese unites with the silicate to form manganese silicate ($MnSiO_3$).

Tri-manganese tetroxid (Mn_3O_4) occurs in nature, and is known as hausmannite. It is considered as a combination of manganese monoxid (MnO), and di-manganese trioxid (Mn_2O_3). (Compare with minim and magnetic iron oxid.) It can be produced by heating manganous oxid (MnO) in the air in the

same way that minim or red lead is prepared. It is the most stable oxid of manganese, and requires a high temperature for its decomposition. Heat converts all the higher oxids of the metal into this form. When acted upon by such acids as sulfuric acid, the results are like those produced with the magnetic iron oxid; namely, both manganous and manganic sulfates are produced. It is not probable that the two oxids exist as such in the compound. There are good reasons for regarding the oxid as a manganous salt of an acid corresponding to the oxid MnO_2, having the formula H_4MnO_4. There are many facts that tend towards this explanation. The reader is referred to larger works for their discussion.

Manganese trioxid, or more properly manganic anhydrid (MnO_3), is quite unstable, and is formed when potassium permanganate is decomposed by sulfuric acid heated to about 45°. It is a dark red liquid which is soluble in water. The product of this solution is probably manganic acid (H_2MnO_4) corresponding to the manganates of (*e*) and (*f*) of the last experimental study. When heated, some of the oxid is volatilized, producing the violet vapor often seen when a permanganate is decomposed by sulfuric acid. The manganates are all powerful oxidizers. In presence of an acid, the manganese is reduced to the "ous" condition. Each molecule consequently yields two atoms of oxygen.

Permanganic anhydrid (Mn_2O_7) is the highest oxid of manganese. It can be prepared from potassium permanganate by the action of sulfuric acid at low temperatures. It is a greenish, heavy liquid that decomposes explosively when heated. It forms an acid when dissolved in water known as permanganic acid (which see).

(*b*) **Hydroxids.** — Divalent manganese forms a hydroxid in the usual manner. It is a white compound that rapidly absorbs oxygen from the air, forming the basic manganic hydroxid (MnOOH), which is brown in color. The normal manganic

hydroxid is insoluble, and is therefore produced by precipitation. This hydroxid dissolves in acids, forming the unstable manganic salts.

(*c*) **Salts.** — As has been already noticed, manganese forms both manganous and manganic salts, *i.e.* salts in which it is either divalent or trivalent. Like chromium, iron, and several other metals, this element acquires acid characteristics the higher is its valence. Its most stable salt compounds are those in which manganese has either its highest or its lowest valence. Manganous salts are readily formed by the general methods already given. (See page 159.) All but the weakest acids form manganous salts, while only the strongest acids form manganic salts. The principal salts are the chlorids, sulfates, carbonates, and sulfids. The salts are generally colored, and the manganous compounds nearly always pink or red.

Manganous Chlorid ($MnCl_2$); Crystals ($MnCl_2 . 4 H_2O$). — This salt is produced in large quantities in the preparation of chlorin from manganese dioxid. This product was, until a comparatively recent time, regarded as a waste product. However, by the Weldon process, the manganese serves again to set free the chlorin of hydrogen chlorid, which is itself a waste product in sodium carbonate manufacture. Calcium oxid (lime) is added to the chlorid in solution, which forms with the manganese the hydroxid. This compound is readily oxidized in the air, and in the presence of calcium oxid forms calcium manganite. The result is a practical regeneration of manganese dioxid, which sets the chlorin free from more hydrogen chlorid. The reactions are commonly represented thus: —

$$MnCl_2 + Ca(OH)_2 = CaCl_2 + Mn(OH)_2;$$

$$2\,Mn(OH)_2 + O_2 + 2\,Ca(OH)_2 = 2\,CaO.MnO_2 + 4\,H_2O;$$

$$CaMnO_3 + 6\,HCl = Cl_2 + CaCl_2 + MnCl_2 + H_2O.$$

An examination of these reactions will show that the manganese is at the end of the reactions in the form of a chlorid, and can therefore be used again by repeating the process. The restoration process is one of oxidation, and the oxygen may be furnished by oxidizing agents as well as by the air.

Two other chlorids are known: manganic chlorid ($MnCl_3$) and manganese tetrachlorid ($MnCl_4$). They are unstable, and readily become the manganous salt.

Manganous Sulfate ($MnSO_4$); Crystals ($MnSO_4.5\,H_2O$). — Manganous sulfate is produced in the preparation of oxygen from manganese dioxid. It crystallizes in pink crystals from water solution at ordinary temperatures. The amount of the water of crystallization varies with the temperature at which the crystals are produced. At 25°, 4 molecules of water are found in the crystals for each molecular proportion of the sulfate. At less than 6° crystals are formed containing 7 molecules of water. The three kinds of crystals are different in form and color. The facts in reference to the formation of the crystals just referred to are, in general, true of other crystallizable substances. For example, copper sulfate ($CuSO_4$) is grayish white in color; $CuSO_4.5\,H_2O$ is blue.

Manganic sulfate is produced when manganese dioxid is dissolved in sulfuric acid, the mixture being not heated above 100°, or when the lower oxid (Mn_2O_3) is dissolved in this acid at low temperatures. (It is a general fact that the higher oxids of manganese, when heated with acids that dissolve them, give up all of their oxygen but one atom.) The salt is a green amorphous powder which forms crystalline double salts of the same general formula as that of the alums. Manganous sulfate also forms double salts corresponding to those of ferrous sulfate. For example, with sodium the salts are $MnSO_4.Na_2SO_4.6\,H_2O$ and $Mn_2(SO_4)_3Na_2SO_4.24\,H_2O$.

Manganates and Permanganates. — The methods of producing these compounds have already been given. The essentials

of the process are (*a*) the presence of some powerful oxidizer that can be made to act at high temperatures, and (*b*) the presence of a strong basic element to unite with the higher manganese oxid when it is formed. The manganate is produced under these conditions. The manganates have a composition similar to that of the chromates and sulfates; *i.e.* the "acid group" is "MnO_4," which is divalent. This group enters into all manganates in the same way that the group "SO_4" is characteristic of all sulfates. The salts of manganic acid are all insoluble except those of the alkali bases. The latter salts are the principal manganates.

The manganates are used, principally, as oxidizing agents. It is this capacity to furnish oxygen in the nascent state that determines their uses as disinfectants. They rapidly oxidize organic matter, and consequently are used to completely decompose such putrefying matter.

As has been shown, permanganic acid may be produced by the action of water on permanganic anhydrid (Mn_2O_7). The usual method for its preparation is first to produce barium permanganate, and then treat this salt with dilute sulfuric acid. The reaction is: —

$$Ba(MnO_4)_2 + H_2SO_4 = BaSO_4 + 2\,HMnO_4.$$

The barium sulfate thus formed is insoluble, and is separated by filtration. The red solution of the permanganic acid can be concentrated by evaporation at low temperature in vacuo. It is a very unstable compound, that decomposes when heated, or when it is exposed to the light. The principal salts of the acid are those of the alkali bases. The methods for preparing these salts have been employed in the experimental study.

The permanganates are more stable than the manganates, and consequently generally take their place as oxidizers. They are generally used in acid solution, since the acid aids in decomposing them, and also unites with the base of the

permanganate and with the manganese. The permanganate thus gives up, for every molecule, 5 atoms of oxygen. (See reactions already studied.) Sulfuric acid is the acid commonly used. In alkaline solution only three atoms of oxygen are given off. In this case the base, — potassium, for example, — if set free from the salt in the presence of water, must become potassium hydroxid. It has been seen, however, that potassium hydroxid and other strong bases tend to form manganites; for example, K_2MnO_3. This may or may not be decomposed into the dioxid according to the conditions. For example, some of the products of oxidation may be acid, and the potassium unites with this acid. The decomposition may be represented thus: —

$$2\,KMnO_4 + H_2O = 2\,KOH + 2\,MnO_2 + O_3;$$

$$6\,KMnO_4 + 2\,KI = 2\,HIO_3(2\,KIO_3) + 6\,KOH + 6\,MnO_2.$$

In the latter reaction, an acid, HIO_3, is formed which unites with a portion of the alkali produced. If the solution is alkaline, manganese dioxid (MnO_2) or some corresponding manganite is always formed.

The alkali permanganates are used as disinfecting agents and in volumetric quantitative chemical analysis. The change of the highly colored solution to a colorless one marks very distinctly the end of the reaction.

NICKEL.

Occurrence and Distribution. — Nickel does not occur free in nature, except in meteors, but is combined principally with sulfur and with arsenic. The principal ores are known as Kupfer-nickel or Niccolite (NiAs) and nickel glance ($NiAs_2.NiS_2$). Nickel is associated with iron, cobalt, and

arsenic in a large number of ores. An ore of considerable importance is nickel silicate. The occurrence of nickel alloyed with iron in meteors is so characteristic that the fact of its presence in a sample of mineral iron is considered conclusive evidence of the meteoric origin of the iron.

Nickel is not very abundant nor are its ores widely distributed in workable quantities. It is found in the Ural Mountains, Bohemia, New Caladonia, in Canada, and the United States.

Preparation. — Nickel is rarely prepared entirely free from other metals. In fact, it has been claimed recently, that what has been called nickel is a mixture of this element with another element which has not yet been fully described. However this may be (and it is doubted by equally good authority), it is quite difficult to separate the metal from those that generally occur with it.

The method, in general, consists of several distinct steps. (*a*) The ore, *e.g.* niccolite, is roasted, by which the arsenic and sulfur are mostly removed, in the usual combination, and the nickel is left as an oxid. If the ore were pure niccolite or nickel glance, the separation of the metal could be easily accomplished. (*b*) By heating the oxid mixed with carbon to a high temperature when the usual reaction between carbon and metallic oxids would occur. But there are present in most cases such metals as copper, bismuth, antimony, iron, cobalt, etc. These metals are removed (*c*) by a somewhat complicated process, the main features of which are the solution of the roasted mass, of (*a*), in hydrochloric acid, the precipitation of the copper, etc., by hydrogen sulfid, the separation of the iron by ammonium hydroxid, the conversion of the nickel into nickel hydroxid, and the decomposition of this compound by carbon.

Experimental Study, No. 27. — (*a*) Examine the nickel for physical properties. (*b*) Test small pieces of nickel with a magnet, comparing it with iron. (*c*) Heat slowly a piece of the bright metal in the air. (*d*) Study the actions of the

acids on the metal. Note the color of the solution and the salts.

Physical Properties. — Nickel is a silver-white metal, nearly as hard as iron, and is, therefore, capable of taking a high polish. The metal is more tenacious than iron, and is quite ductile and malleable. It is magnetic, although less so than iron, but unlike iron, it loses this property at temperatures above 350°. Its specific gravity is 8.9.

Chemical Properties. — Pure nickel is not readily produced, owing to the metals that are associated with it in its ores. Its oxalates and carbonates are insoluble, and therefore these salts can be prepared quite pure. These salts are ignited in an atmosphere of hydrogen, and a fairly pure metal is thus prepared. Nickel does not oxidize readily at ordinary temperatures. In moist air, it is more readily tarnished, somewhat resembling copper in this respect. It is said that cast nickel is not at all oxidized in the air at ordinary temperatures, and only slightly so even at high temperatures. It is not easily attacked by hydrogen sulfid, and is, consequently, quite resistant to ordinary air. Nickel slowly dissolves in both hydrochloric and sulfuric acids, forming the corresponding salts. Nitric acid readily oxidizes it and forms nickel nitrate.

Atomic Mass and Valence. — Nickel forms no volatile compounds, and, consequently, no aid to the determination of atomic mass can come from this source. Its specific heat is .108, which corresponds to an atomic mass of 59.2. The atomic mass obtained by different investigators is more variable for this element and for cobalt than for any other elements. These results have varied from 56 to 59 +. Recently this has been explained by Gerhardt Krüss, to which reference has already been made. Other chemists question the conclusions that he has derived from his results. The true atomic mass of nickel is, therefore, not accurately known, but 58.9 is the commonly accepted number.

Nickel forms but one sulfate; or, in other words, nickel cannot divide the hydrogen of sulfuric acid. The amount of nickel in nickel sulfate on this basis is 58.7 parts to 96 parts of sulfur and oxygen. This being considered the atom of nickel, the valence is 2, or the element is bivalent. A study of the other compounds, like the halogen salts, establishes the bivalent character of the element.

Name and History. — The element nickel was discovered in a mineral that was supposed to contain copper because of its copper color. No copper was obtained, but a new metal was found in the mineral by Cronstedt in 1750. It was named nickel from the mineral just mentioned, which for a long time had been known as Kupfer-nickel. *Nickel* originally meant that which was worthless, and was applied to this substance because it was found to contain no copper.

Uses. — Nickel has become, within a few years, one of the most useful of the metals. It is said that its uses as a protector and beautifier of other metals has added an entirely new industry that employs over thirty thousand men. Although not as brilliant and attractive as silver, yet it is capable of receiving a high polish and is harder and at the same time is much cheaper than the latter element. As a plating, it is readily deposited on most metals and especially so on iron. It is deposited on iron by the action of an electric current, the article to be covered being placed in a solution of a nickel salt, usually of nickel ammonium sulfate. The nickel is supplied from nickel plates, which are attached to the positive pole of the current. The object is connected with the negative pole. The nickel sulfate is decomposed, and sulfuric acid is formed, the nickel being deposited on the object to be plated. The acid attacks the nickel pole and restores an equivalent amount of the sulfate. The action accordingly goes on until the nickel pole has been dissolved. Iron objects, whose surfaces are chemically clean, become coated with nickel when placed in solutions of nickel salts.

Nickel forms alloys with nearly all metals, many of which are of great value. It has recently been discovered that a small per cent of nickel in steel (or iron) adds greatly to its rigidity and toughness. Nickel steel has become, therefore, an article of great commercial importance. Such alloys as the nickel five cent coin, German silver "white metal," are examples of useful alloys. The more nickel there is present in the alloy, the whiter and harder it is. German silver and the nickel coin have a constant composition. The former contains of each, zinc and nickel, 20 per cent; and of copper, 60 per cent. The latter contains 75 per cent of copper, and 25 per cent of nickel.

Experimental Study, No. 28. — (*a*) Heat some of the nickel nitrate produced in the previous study to the temperature of the lamp. Heat until the action is complete. What gas escapes? What is the residue? Why? Suppose the compound had been either the carbonate or hydroxid, what would have been the volatile and the solid products? What is the effect, in general, of heating the compound just mentioned? Note the color of the residue. Suppose the residue were placed in a tube and heated to red heat and a current of hydrogen were passed over it, what result would you expect?

(*b*) Study the reaction of the usual reagents on the solution of a salt of nickel, *e.g.* nickel sulfate. Note the solubility of salts in the table of solubilities and write the reactions. The precipitates are all normal except the carbonate, which is basic and variable in composition. The normal carbonate is formed when a soluble salt is added to an excess of sodium acid carbonate. KCN dissolves nickel cyanid when added in excess, forming compounds similar to potassium ferro-cyanid ($K_2Ni(CN)_4$). Boil the solution of the cyanid in a solution of NaClO. (This reagent is prepared by adding Na_2CO_3 to a clear solution of bleaching-powder as long as a precipitate is formed. Filter out the precipitate. The clear solution is the reagent.) What kind of a reagent is NaClO? The precipi-

tate is $Ni(OH)_8$. Test the solubility of the sulfid in dilute HCl and in concentrated HCl.

Note the solubility of nickel hydroxid in ammonium hydroxid. What other base gives the same colored solution?

(*c*) Make a borax bead, and while hot bring it in contact with some solid compound containing nickel, like the hydroxid or nitrate. Now heat in the oxidizing flame of the lamp. Note the color of the bead while hot (not red hot) and when cold. (If the bead is too deeply colored, add more borax and fuse again. If not sufficiently colored, add more of the nickel compound.) Heat the bead in the reducing flame and note any changes. How can the reducing flame affect the nickel compound? In what combination will the nickel be if heated in the oxidizing flame? Suppose the nickel compound had been the sulfid, what changes occur when the bead is made? What changes occur when the borax bead is made? How is the nickel combined in both cases of heating?

(*d*) Heat, with a blow-pipe flame, a nickel salt on charcoal, covering the salt with Na_2CO_3. Separate off the mass and dissolve away the excess of Na_2CO_3. Examine the dark residue with the magnet. Write the reaction, using nickel hydroxid or nitrate. What part does the charcoal play?

Compounds of Nickel.

(*a*) **Oxid and Hydroxid.** — Nickel readily forms but one oxid and its corresponding hydroxid. Both are insoluble in water, but dissolve readily in most of the acids that form soluble nickel salts. The oxid (Ni_2O_3), nickelic oxid, has been prepared, but it does not form any stable salts. The corresponding hydroxid is produced when nickel salts are treated with a strong oxidizing agent like a hypochlorite or like chlorin in an alkali solution. Like the oxid, it does not form stable salts.

(*b*) **Salts of Nickel.** — The salts of nickel all correspond to the monoxid (NiO). The soluble salts are generally apple-green in color, and when crystallized they contain water of crystallization. Those deprived of the water of crystallization are yellow. The anhydrous salts absorb ammonia, usually the same number of molecules as the hydrous salt contained molecules of water. The principal salts are the chlorid ($NiCl_2.6\,H_2O$), the nitrate ($Ni(NO_3)_2.6\,H_2O$), and the alum, nickel ammonium sulfate ($NiSO_4(NH_4)_2SO_4.6\,H_2O$).

Nickel sulfid (NiS) is a black insoluble substance found in nature in hair-like crystals, known as millerite. It is also produced by the action of an alkali sulfid on a soluble salt of nickel.

COBALT.

Occurrence and Distribution. — Cobalt occurs associated with nickel in many of the ores of the latter metal; in fact, the two elements are rarely found separate in nature. The principal ores are cobaltite ($CoAs_2.CoS$) and smaltite ($CoAs_2$). Like the ores of nickel, several other metals are found with those of cobalt, such as iron, bismuth, manganese, etc. Native cobalt is found in small quantities in meteors.

Cobalt ores are not widely distributed, but are found in the localities given for nickel.

Preparation. — The same difficulties arise in obtaining cobalt that have been described under nickel.

The processes are quite similar in reference to the elimination of all the elements except the nickel. The cobalt is separated from this element by treating the solution from which other elements have been removed with a solution of bleaching-powder, which precipitates the cobalt before acting on the nickel as cobaltic hydroxid ($Co(OH)_3$). The metal is obtained

from this compound by heating it with carbon or in hydrogen gas. The hydroxid is more commonly used than is the free metal itself.

Physical Properties. — Cobalt resembles iron in many respects. It is, however, a little harder and heavier, its specific gravity being 8.7. The metal is very tenacious, ductile, and malleable. It is silver-white in color, especially so when deposited by electricity. The samples of the metal commonly seen have a reddish appearance. Unlike nickel, it does not lose its magnetic property even at red heat. Nickel becomes non-magnetic at temperatures above 350°. Its magnetic power is less than that of iron.

Chemical Properties. — Cobalt is less readily attacked by the atmosphere than is nickel. At white heat, it is oxidized to an oxid of the same form as are manganese, iron, etc., under the same conditions; namely, to Co_3O_4 called cobaltous-cobaltic oxid. Like iron, it has the property of uniting with carbon, forming a quite fusible compound. Nitric acid readily oxidizes the metal, and converts the oxid formed into the soluble nitrate. Sulfuric or hydrochloric acid dissolves the metal, forming the usual products; but the action is slow, even when they are aided by heat.

Name and History. — Cobalt was first separated from its ores, in 1733, by Brandt, who named it kobalt-rex. The name had been applied for a long time to certain ores whose general appearance suggested that they contained valuable metals. The miners regarded these ores very much as they did the Kupfer-nickel mineral, and named them for the evil spirit that they believed lived in the mines. Compounds containing cobalt were known and used in the early times for coloring glass. The metal has no particular uses, although it might well take the place of nickel, since it is more resistant to atmospheric agents.

Atomic Mass and Valence. — The general statements made

under this topic in the study of nickel apply equally well to cobalt. The atomic mass of cobalt is generally taken as 59.67. It is bivalent generally, although its compounds, when trivalent, are much more stable than are those of nickel under the same conditions.

Experimental Study, No. 29. — Follow the directions given under Experimental Study, No. 28, using cobalt nitrate instead of nickel nitrate, omitting (*d*). Mix some aluminium hydroxid with cobalt hydroxid, and heat them strongly on charcoal in the blow-pipe flame. Note the color of the residue. In what condition are the two hydroxids? What is the first change that occurs? Has a chemical change occurred in reference to the bases? Which is more basic, aluminium or cobalt? How does aluminium oxid act towards such strong bases as KOH? (See under ALUMINIUM.) Suppose the nitrate of cobalt had been used, explain the changes as the mass is heated.

Compounds of Cobalt.

The general remarks made under nickel apply to cobalt compounds.

(*a*) **Oxids and Hydroxids.** — Cobalt forms three oxids, namely, cobaltous, cobaltic, and cobaltous-cobaltic oxids, — CoO, Co_2O_3, Co_3O_4. The first two oxids form salts, but the cobaltous oxid is more strongly basic.

The higher oxids are prepared by heating the cobaltous oxid in the air. For example, if cobaltous nitrate is heated to a temperature sufficient to just decompose it, cobaltous oxid is the one of which most is formed. At a little higher temperature, cobaltic oxid is produced, and at still higher temperature, the cobalto-cobaltic oxid is formed. The higher oxids are easily reduced to cobaltous oxid by hydrogen at a temperature below 300°.

The fixed alkali bases form with cobaltous salts a basic compound which, by boiling, becomes the normal hydroxid. This

hydroxid acts in the air like those of ferrous and manganous hydroxids; *i.e.* it takes up oxygen and becomes the cobaltic compound.

(*b*) **Salts of Cobalt.** — Cobaltous salts are generally quite stable. The water soluble salts crystallize in red crystals. The solutions are rose-red. The anhydrous salts are often a deep blue, and this is especially true of cobaltous chlorid. This salt forms an intense blue solution when dissolved in absolute alcohol. The sympathetic inks are solutions of cobaltous chlorid. When this solution is used as an ink, it leaves an almost imperceptible mark after the ink has partially dried. If now the paper is completely dried, the salts become anhydrous and sufficiently blue to be distinctly seen. On absorbing moisture again, the writing becomes invisible.

The principal salts of cobalt are the chlorid ($CoCl_2.6\,H_2O$), the nitrate ($Co(NO_3)_2.6\,H_2O$), the sulfate ($CoSO_4.7\,H_2O$), and the sulfid (CoS).[1]

Cobalt sulfid is of interest because it is the combination in which cobalt is found in the third group separation. It is insoluble in water and, in the cold, in dilute hydrochloric acid. It is soluble in the hot acid. Although the sulfid is insoluble, it is not formed by hydrogen sulfid acting upon any of its soluble salts except the acetate. The reason for this is seen when it is remembered that this reagent forms, as one of the products of the reaction, the acid corresponding to the salt of the metal acted upon. (See later on under discussions of groups.) A soluble sulfid, like ammonium sulfid, readily forms this sulfid.

A substance of considerable commercial importance is known as smalt. It is produced by fusing together cobalt oxid

[1] The student should, in the study of each metal, answer such questions as the following: Given cobalt chlorid, how would you prepare cobalt sulfate? Given cobalt sulfid, how could you prepare cobalt phosphate? See methods for preparing salts, page 159.

(usually the impure compound) with silicon dioxid and potassium carbonate. A chemical reaction occurs in which there is formed potassium silicate (K_2SiO_3) and some cobalt silicate ($CoSiO_3$). The whole becomes fused into a homogeneous mass of an intense blue color, the intensity of which depends on the amount of the cobalt salt present. In smalt the color is a very deep blue. This glass-like substance is finely powdered and used as a pigment. A similar reaction was produced in the last study in case of the borax bead. Here the cobalt metaborate ($Co(Bo_2)_2$) was formed instead of the silicate.

Another blue substance known as cobalt-ultramarine, or Thenard's blue, is produced when cobalt oxid is heated with aluminium oxid (Al_2O_3). The production of the blue compound is often used to detect the presence of either cobalt or aluminium compounds. It is probable that cobalt aluminate is formed, $Co_3(AlO_3)_2$. In the formation of cyanids, cobalt acts like iron. For example, potassium cyanid precipitates cobalt cyanid, which dissolves in excess of the reagent, forming $K_2Co(CN)_4$. Potassium cobaltous cyanid.

Potassium cobaltic cyanid ($K_3Co(CN)_6$) has been prepared. The cyanid acids of cobalt corresponding to ferro- and ferricyanic acid have been separated. This is done by producing some insoluble cobalto- (or -ic) cyanid, like copper, and then decomposing it by hydrogen sulfid.

ZINC.

Occurrence and Distribution. — Zinc is rarely, if at all, found free in nature. As might be expected from what is true of most of the other metals, zinc occurs combined with sulfur, forming the mineral called zinc blende or sphalerite. It is also found as zinc carbonate, smithsonite, as zinc silicate, calamine,

and as zinc oxid or zincite. There are several other minerals that contain zinc, some of which, like franklinite, which is the oxid of iron and zinc, are occasionally used as ores. The ores of zinc are quite widely distributed. They are found in Europe, in Sweden, Poland, Belgium, in England, and in the United States, in New Jersey, Missouri, Iowa, and in fact it is quite generally found where lead and copper ores occur.

Preparation. — The principal ores of zinc are the sulfid and the carbonate. This naturally suggests that the first treatment in the preparation of the metal should be the roasting of the ore. The roasting of the ore drives off moisture and oxidizes the sulfur and the metal. The final reduction is the removal of the oxygen, from the oxid by the usual reagent, carbon. The zinc is vaporized and condensed as a fine powder. Prepared in this manner it often contains such metals as arsenic and lead, which are carried over with it in the distillation. Commercial zinc is purified by several methods, such as repeated distillation, and again by the electro-deposition from a solution of zinc sulfate made alkaline by ammonia.

Experimental Study, No. 30. — (*a*) Examine a stick of cast zinc for structure and physical properties. (*b*) Place a small bit of zinc in the deflagrating-spoon and heat to the temperature of the lamp. Note the changes that occur. Heat another piece on charcoal, using the oxidizing blow-pipe flame. What is the deposit on charcoal? Carefully heat it again and note changes in color. These are quite characteristic of zinc.

(*c*) Heat some zinc tartrate ($ZnC_4H_4O_6$) in a test-tube to complete decomposition. Cool partially, and stopper the tube tightly until cold. Allow the residue to fall out of the tube to the floor. In what condition is the zinc? Write the reaction, accounting for all of the elements. What is the black residue?

(*d*) Study the action of acids on zinc. What are the compounds formed? Compare these reactions with those produced

by these acids on the metals already studied. The solution may be evaporated to crystallization.

(*e*) Carefully weigh out about one gramme (some definite mass, however) of pure zinc. Fill a 400–500 cc. gas bottle with water acidulated with H_2SO_4 (1–12). Invert the bottle in the trough, using just water enough to cover the mouth of the bottle. Now place the weighed zinc under the bottle, and allow the action to continue until the zinc is wholly dissolved. (It may be necessary to place the zinc in contact with a piece of platinum foil, especially if the zinc is quite free from impurities.) When the action is complete, measure the volume of the hydrogen according to the method previously used, observing the necessary conditions; namely, that the gas be cooled to the temperature of the room, and that it be under the pressure of the atmosphere at the time of reading. Take the barometer and thermometer readings and compute the volume of the gas at 0°, and thus determine the mass of the hydrogen set free. Write the reactions. Making the mass of hydrogen unity, what does the mass of the zinc used become? Since zinc sets free all of the hydrogen of the acid, how much zinc corresponds to the two atoms of hydrogen? This is the smallest amount of zinc found in any molecule.

There are at least two compounds containing zinc whose vapor densities have been carefully determined. Of these compounds, one contains 48.35 per cent of zinc and 51.643+ per cent of chlorin, and has a vapor density of 67.87. The other compound contains 68.52 per cent of zinc, 25.183 of carbon, and 6.296+ of hydrogen, and has a vapor density of 47.65. Determine the amount of zinc in these molecules. Compare the amounts with the equivalent of two atoms of hydrogen.

Physical Properties. — Zinc presents many characteristic physical properties. It is crystalline in structure when it is cast. This structure affects its specific gravity, since the cast

zinc has a specific gravity of 6.8, while rolled zinc is 7.2. Zinc is quite malleable at temperatures between 100° and 150°. As the temperature is raised above 150°, the malleability grows less, and at about 200° it becomes very brittle, and may be readily pulverized into fine powder. Zinc fuses at 423° and vaporizes at 1040°. The vapor density of zinc is 32.5+. It is therefore in the atomic condition when in the form of vapor.

Chemical Properties. — Crystallized zinc is not readily oxidized in the air at ordinary temperatures. At its vaporizing temperature it oxidizes rapidly, producing a brilliant white light. In moist air, carbon dioxid and water form a basic carbonate which is adherent to the zinc, and thus prevents further change. Its affinity for oxygen is so great at high temperatures that it decomposes water, setting hydrogen free and forming zinc hydroxid.

The action of acids upon zinc varies, in general, with the concentration of the acid, the temperature at which the action occurs, and the purity of the metal. Usually, however, a salt of zinc is formed, and hydrogen is set free. The different products formed under the conditions just mentioned are, in many case, due to the secondary action of the hydrogen, or possibly to the reducing action of the zinc itself; for example, on sulfuric acid. The production of SO_2 can be explained by referring to the direct action of zinc in removing oxygen from the acid. (See under COPPER and other metals.) Concentrated sulfuric acid acts very slowly, if at all, on zinc. This is probably due to the fact that zinc sulfate is insoluble in undiluted sulfuric acid. The action of sulfuric acid on pure zinc is always slower than it is on the impure metal. The impurities appear to form electrical couples, which aid in the solution. The fact is illustrated by placing the pure zinc in contact with a piece of platinum or other metal, when a much more rapid evolution of hydrogen at once begins.

Nitric acid is completely reduced by the hydrogen set free, the nitrogen forming ammonia, the lowest reduction of nitrogen that is possible.

Potassium and sodium hydroxid act upon the metal zinc very much in the way they do upon aluminium; *i.e.* they dissolve it with the evolution of hydrogen and the formation of unstable compounds, called zincates of the general form R_2ZnO_2.

Name and History. — Zinc was employed from very early times in an alloy with copper, which we now know as brass. In China, the method of separating the metal was known and used for a long time before the process was employed in civilized countries. Brass was made in Sweden, during the fifteenth century, from the native carbonate, then called calamine. Brass was produced by heating together metallic copper and zinc ores. It is probable that Paracelsus prepared zinc from calamine, but its production in large quantities is a modern industry, beginning about the year 1800, although before this time, as early as 1740–50, it was prepared by processes that were kept secret. The metal was named by Paracelsus.

Atomic Mass and Valence. — As has been seen under the last study, 65 parts of zinc correspond to two atoms of hydrogen; also that the amount of zinc in the two gaseous molecules that have been studied corresponds to this amount of zinc. Zinc oxid has been found to contain 65 parts of zinc to 16 parts, or one atom, of oxygen. The atomic mass of zinc is, therefore, 65, and its valence is 2. The specific heat of zinc, .093, corresponds approximately to this atomic mass.

Uses. — The industrial applications of the metal zinc are very numerous. The properties already given make it useful in the form of sheets for covering and protecting from atmospheric agencies, roofs, and in architectural ornamentation, etc. It is used in nearly every form of galvanic battery as the positive pole. In fact, the actual cost of using most batteries is largely controlled by the cost of zinc.

Zinc forms a large number of useful alloys. Among these may be mentioned brass, the alloy of zinc and copper. The character of the brass may be much modified by varying the proportion of these elements. Other alloys have been mentioned in the study of the other metals.

Another use of zinc is that of coating or protecting iron to prevent it from oxidizing (rusting). The product is called galvanized iron. The zinc is deposited by dipping chemically cleaned sheets of iron in molten zinc, somewhat as ordinary tinned iron is made. No electric current is necessary.

Finely divided zinc is a powerful reducing agent. (See study of ZINC TARTRATE.)

Experimental Study, No. 31. — (*a*) Use the solution of zinc sulfate made in the last study (or a solution of the crystallized salt) and study the action of the usual reagents on it, following the usual directions. The precipitates formed are all normal except the carbonate, which has a variable composition, depending on the conditions under which it is produced. The precipitated carbonate of commerce is usually represented by the formula $ZnCO_3.3\,Zn(OH)_2$.

Note the action of the hydroxids, adding the reagent drop by drop, and boil the solution after adding an excess of the reagent. Alkali zincates are produced (R_2ZnO_2). The precipitate is the hydroxid.

Note the action of H_2S in neutral, acid (HCl and $HC_2H_3O_2$), and alkaline (ammonia) solutions.

(*b*) Heat some zinc carbonate on charcoal and note the deposit. What is it? Wet it with a solution of cobalt nitrate and heat again. What two compounds are left on the charcoal as the result of the heating? This compound is called green cinnabar, Rinman's green, and green vermilion. It is probably cobalt zincate. (See POTASSIUM ZINCATE. Write the reaction.)

(*c*) Slightly acidify a solution of copper sulfate and add a small piece of zinc. Explain the reaction. Where is the zinc?

Solutions of other metallic salts may be used in the same manner. For example, solutions of iron, lead, etc., salts.

Compounds of Zinc.

(*a*) **Oxids and Hydroxids.** — Zinc is bivalent in all of its compounds, and hence the oxid has the formula ZnO. The oxid is commercially prepared by the usual methods; namely, by oxidizing the metal or by decomposing the carbonate by heat. It is known as "zinc white," and is used as a pigment in oil painting. It is used in many cases in preference to "white lead," since its sulfid is white and, therefore, is not visibly affected by hydrogen sulfid.

Zinc hydroxid is only slightly soluble in water, but is soluble in the alkali hydroxids, forming soluble alkali zincates. These zincates are reprecipitated from their alkaline solution by boiling. The hydroxid is faintly alkaline to litmus, although water dissolves but 1 g. in 554,000 g. of water.

(*b*) **Salts of Zinc.** — Zinc is generally basic although it forms salts with the strong bases, as has just been pointed out. It forms salts with most of the inorganic, and many organic, acids that are crystalline when soluble.

The soluble salts are all poisonous, and hence the metal cannot be employed for vessels that are to be used in preparing food or that are to contain preserved fruits, since the acid of the fruit dissolves the zinc forming soluble salts.

The principal salts of zinc are the chlorid, sulfate, carbonate, and sulfid. The salts are generally acid to litmus paper.

Zinc Chlorid ($ZnCl_2$); Crystals ($ZnCl_2.H_2O$). — Beside the usual methods for preparing zinc chlorid, it is formed by heating the powdered metal in a stream of chlorin gas, and by mixing zinc sulfate and calcium chlorid and heating the mass to the temperature of volatilization of the zinc chlorid that is formed.

Zinc chlorid is volatile at temperatures above 680°. The

vapor density of this compound is 67.8, corresponding to the formula $ZnCl_2$. (See page 229.)

Zinc chlorid possesses many valuable properties, among which are its affinity for water, making it useful as a drying agent; its powerful caustic and antiseptic and disinfecting properties, which render it valuable in surgery and as a general disinfecting and preserving agent. For example, wood is preserved by soaking it in a solution of this salt. A solution of the salt is used by tinners in soldering. There is always a little free acid in the solution which dissolves any oxid from the surface of the metal. The zinc chlorid forms a soluble double salt with the chlorid that has been produced. This leaves a chemically clean surface of metal to alloy with the solder. The chlorid forms a number of double salts with other chlorids, such as ammonium chlorid ($ZnCl_2.(NH_4Cl)_2$). These salts are sometimes regarded as chloro-zincates; *i.e.* as corresponding to an acid, H_2ZnCl_4. Accordingly the double salt with potassium is K_2ZnCl_4.

Zinc is so weak a base that the chlorid is decomposed by water at temperatures of about 135°, forming a basic chlorid (ZnOHCl).

$$ZnCl_2 + H_2O = Zn\begin{matrix}\diagup Cl \\ \diagdown OH\end{matrix} + HCl.$$

At higher temperatures the decomposition is complete, and zinc oxid is the final product.

Zinc Sulfate ($ZnSO_4$); Crystals ($ZnSO_4.7\,H_2O$). — Zinc sulfate is one of the compounds that was known to the early chemists, and was named by them *white vitriol* to distinguish it from blue and green vitriols, copper and ferrous sulfate respectively. The substances were so named from their glassy appearance.

Zinc sulfate is commonly prepared from the native sulfid, zinc blende, by slowly roasting it, and treating the residue with

water, which dissolves the sulfate. The salt is obtained from this solution by evaporation and crystallization. Six of these molecules of water are driven off at 100°, but the last one requires low red heat for its removal.

The salt is used in medicine and as a mordant in dyeing. It forms double salts containing six molecules of water; for example, zinc and sodium sulfate ($Na_2SO_4.ZnSO_4.6\,H_2O$).

Zinc Sulfid (ZnS). — Zinc sulfid is found in nature, and is known as zinc blende. Like most native compounds, it is not pure, but contains iron and cadmium. The native sulfid is always colored, but the precipitated form has a dirty white color, and it is the only white sulfid that is readily produced by precipitation. It is soluble in hydrochloric acid, and in most of the common acids, except acetic acid. Accordingly it is only partially precipitated by hydrogen sulfid except from its acetate solution. An examination of this reaction on the basis that the sulfid is insoluble will illustrate this fact for this base, and also for all bases whose sulfids are soluble in an acid corresponding to the salt acted upon by hydrogen sulfid.

$$ZnSO_4 + H_2S = ZnS + H_2SO_4;$$
$$FeCl_2 + H_2S = FeS + 2\,HCl.$$

Both these sulfids are readily dissolved in either of the acids that are formed, and consequently, although the sulfid is insoluble in water, no precipitate, or only a slight one, is formed under these conditions.

In separating zinc from other metals, it is precipitated by ammonium sulfid in alkaline solution. The other salts of zinc are of little importance, and all the necessary facts in reference to them have been learned under the last experimental study.

Experimental Study, No. 32. — (*a*) Study a solution containing salts (say the sulfates) of cobalt (or nickel), manganese, and zinc for the purpose of separating and recognizing each of the bases, using the facts learned in the studies of these ele-

ments. $(NH_4)_2S$ will produce what compounds? Write the reactions. After thoroughly washing the precipitate add dilute HCl without warming. What effect will this have on the compounds? How are zinc and manganese combined? To the HCl solution add cold solution of KOH (reagent), making the solution strongly alkaline. Why not heat the solution? (See (*a*) of No. 31.) Where is the zinc now? Where the manganese? Recognize each of bases.

(*b*) Suppose a solution to contain salts of the bases iron, chromium, and aluminium in addition to those mentioned in (*a*), how could they be separated and recognized? (See study on page 205.) The student should write out the method employed, remembering that he has studied all the facts necessary for this work.

CALCIUM.

Occurrence and Distribution. — Calcium stands fifth among the elements in reference to its abundance in the earth's crust. It is an active element, chemically speaking, and hence is not found uncombined in nature. Its compounds are widely distributed and are abundant in quantity. The principal compounds are limestone and marble, more or less impure carbonates, fluorspar, or calcium fluorid; gypsum, or calcium sulfate; apatite, or calcium phosphate; and a large number of silicates. Its compounds form the hard parts or skeleton of the vertebrata and the shells and covering of the invertebrata. It is an essential element in fertile soils; not that it is like potassium, essential to the plants themselves, but that it sets up chemical and physical conditions that are practically essential to a fertile soil. The shells of eggs are largely composed of calcium carbonate.

Preparation. — The metal calcium serves no useful purpose, and consequently its preparation is of interest from the chemi-

cal standpoint only. Its great affinity for oxygen prevents its preparation from its oxid by the action of carbon. It is also probable that the infusibility of the oxid aids in preventing this decomposition, since if the oxid were fusible, a more intimate contact could be had between it and the carbon. It is commonly prepared by the action of a powerful electric current on the chlorid of the metal. The chlorid is fused, and in this condition is decomposed by the electric current. The element, being strongly electro-positive, is found at the negative pole of the current. Again, when the chlorid is fused with zinc and sodium, the intimate contact that is produced and the presence of the molten zinc enables the sodium to decompose the chlorid, forming an alloy of zinc and calcium, and sodium chlorid. The calcium is separated from the zinc by distillation.

Properties of Calcium. — Calcium is one of the light metals, having a specific gravity of 1.57. It is quite hard and ductile and can be hammered or rolled into thin sheets. It is yellow, resembling gold, although it more nearly resembles brass in color. Its specific heat is .17. It melts at bright red heat.

Were it not for its active chemical properties, for example, its affinity for oxygen, it would prove a very useful and ornamental metal. It decomposes water rapidly, but less rapidly than does sodium or potassium. The products of this decomposition are correspondingly the same; that is, hydrogen and calcium hydroxid. The element is strongly basic, and consequently is rapidly acted upon by all the acids.

Name and History. — The name of the metal is derived from the Latin word for chalk, *calx*, the substance from which lime was prepared. The element calcium was obtained from *calx* by Sir H. Davy in 1808, the *calx* being first converted into the chlorid from which it was obtained by electrolysis. It was, and is often now, called an alkaline earth metal.

An earth was, according to the alchemist, any substance which resisted the action of water and heat and was not a metal.

They were, like the earth, resistant to the action of two of the most common agents, fire and water. The term included a number of substances that had been discovered from time to time during the period of the early chemists, which possessed the properties just given. Sand, and what we now know as aluminium, iron, and magnesium oxids were included among these earths. In general, these metals have great affinity for oxygen and are separated from it with great difficulty. It was found that these earths might be divided into two classes, on the basis of their having or not having the property of alkalinity. Hence, the elements calcium, barium, and strontium are called the alkaline earths. These latter substances were so resistant to decomposition that they were regarded as elements until Davy in 1808 succeeded in separating them by electrolysis.

Atomic Mass and Valence. — Soon after Davy succeeded in preparing calcium, Berzelius began the study of the element to determine its atomic mass. His results were uncertain, but nothing more definite was done until about 1850. In this examination it was assumed that one atom of oxygen was united with one atom of calcium, or that calcium carbonate when it was heated to temperatures of decomposition was split up into calcium oxid and carbon dioxid (CaO and CO_2). Of course, the fact that carbon dioxid was driven off in decomposition had been known for a long time, and also that calcium oxid was left behind as a solid residue.

It was found that if oxygen is 16, then calcium is 40. This number is the combining mass of calcium, and is accepted as its atomic mass. The specific heat corresponds approximately to this number.

Experimental Study, No. 33.—(*a*) Treat (say) 5 g. of powdered marble with HCl. What gas escapes? What use has been made of this reaction before? What is the compound left in solution? Boil, adding marble as long as it dissolves. Save the solution.

(*b*) Heat to highest temperature possible some finely powdered marble on platinum foil for about ten minutes. Allow it to cool, and transfer to a test-tube and add a few drops of water. Allow to stand a short time. Is there any rise in temperature? Add HCl. Does any gas escape now? What has become of the CO_2? What is the residue?

(*c*) Use the solution made in (*a*), treating portions with the usual reagents, writing the reactions, remembering that calcium is bivalent. The precipitates are all normal salts. Note the difference in the action of the fixed and volatile alkalis on this salt. Note also the action of $K_2Cr_2O_7$. (See BARIUM.)

(*d*) To a fairly concentrated solution of a calcium salt add a solution of $(NH_4)_2SO_4$. Dilute the solution to one-half its concentration and add the same reagent. Note the result. If a precipitate is formed, dilute again and add the reagent. What does this say about the solubility of calcium sulfate? Dilute solutions in the same way, and use $(NH_4)_2C_2O_4$ as the reagent.

(*e*) Place a small lump of lime in an evaporating-dish and add enough water to moisten it. Add more water in small quantities as long as any action occurs. Note the rise in temperature. The hydroxid is formed. Write the reaction. How does this action compare with that between K_2O and water? Add water to a portion of the solid compound, shake well, warm (not boil) if necessary, and allow to stand for ten minutes. Filter and prove the presence of the calcium compound in the solution (see (*c*)). Test also by taste and by litmus. What is the action of CO_2 on this compound? (Reaction?) Why is this a test for CO_2? Boil some of the clear solution. What does the result determine in reference to solubility? Add hydrogen dioxid to a saturated solution of $Ca(OH)_2$. The crystals are calcium dioxid and water ($CaO_2.8\ H_2O$). Write the reaction. What does the dioxid usually become when it is decomposed?

(*f*) Clean a platinum wire, dip it in a solution of $CaCl_2$, and

heat the wire in a colorless lamp-flame. Note the effect on the color of the flame. This result is characteristic, providing no other base is present that colors the flame. Sodium gives a yellow flame under these conditions, and interferes with the test. (See under STRONTIUM and SODIUM.) (To clean the platinum for this test, proceed as follows: Remove all the solid matter from the wire that is possible by washing. Next place in a clean test-tube 5 to 10 cc. of pure HCl. Heat the wire and dip it in this acid, reheating and rewetting, until the flame is no longer colored or only slightly colored.)

Soluble salts of calcium will generally give a result like that of the chlorid. It is best, however, to add HCl to the solid compound, and use the solution as just described.

(*g*) Weigh from 5 to 10 g. of dry plaster of Paris. (Dried by heating to 230° for some time, or until of constant mass. It is probably best to furnish the student a sample so dried.) Place the plaster in an evaporating-dish, and add sufficient water to thoroughly moisten it. Let it stand for twenty-four hours or more, or until dry. Weigh again, and note changes in mass. (It may be dried at temperatures below 76°, and should be dried to constant mass.) Compare this result with the original mass. Suppose that mass of plaster as first weighed becomes 136, what does the change in mass become? For example, suppose that 20 g. of plaster is weighed out, moistened as directed, and, on drying it to constant mass, it weighs 25.36 g. What will this number become if 20 is changed to 136? What is the numerical difference between the two numbers? How many molecules of water is it?

(*h*) To 10 g. of bleaching-powder add 20 cc. of water. Shake thoroughly, and let the mixture stand for a few minutes. Filter, and to a portion of the clear solution add a few drops of HCl. What gas escapes? Review the study of bleaching given in Part I. under CHLORIN.

Compounds of Calcium.

(*a*) **Oxids and Hydroxids.** — Calcium is a strongly basic element, and consequently its oxid is not found free in nature. It is prepared by the usual methods for producing oxids. The commercial oxid, known as lime, is prepared from the native carbonate by heating it to temperatures of bright red heat. The purity of the product, of course, depends on the purity of the native carbonate, which varies from the pure crystallized calcite to quite impure limestone. The pure oxid is often prepared from the pure calcium nitrate, which has been itself prepared from the native carbonate.

Commercial Production of "Lime." — The essentials of a "lime kiln" are non-conducting walls to prevent loss of heat, and a means of supplying sufficient air for the rapid combustion of fuel. The walls of the kiln are usually built of brick. They are often roughly constructed, and must be cooled down after decomposition of the carbonate before they can be emptied and refilled. They are, however, more often so constructed that they can be "run" continuously. Steam is often passed into such a kiln, since the decomposition is more complete if some other gaseous substance is present. (See larger works.)

Calcium oxid is a white infusible substance. (Lime varies from nearly white to a reddish gray.) The infusible property of the oxid makes it useful in the calcium light. For this purpose it is compressed into sticks which are heated to the high temperature of the oxy-hydrogen flame. Under these conditions it glows, and thus becomes the source of light. It is owing to its infusibility that it is used to line furnaces and for crucibles which are to be subjected to the highest attainable temperatures.

The oxid reacts with water, producing calcium hydroxid, and with acids to form salts. It is called quicklime to distinguish it from the hydroxid, which is called "slaked lime."

It has such an affinity for water that it absorbs it from the atmosphere. It also absorbs carbon dioxid, forming the carbonate ($CaCO_3.CaO.CO_2$).

Calcium peroxid or dioxid (CaO_2) is produced as described in the last study. It is easily decomposed by heat, yielding oxygen and calcium oxid (CaO). It does not form salts, but when acted on by acids, it forms salts in which calcium is divalent, and oxygen is finally set free. (Hydrogen dioxid may be formed, but breaks up into the usual products.)

Calcium hydroxid is one of the most useful of chemical compounds. It is a white solid, partially soluble in water, imparting a distinctly alkaline reaction to the solution. One liter of water at ordinary temperatures dissolves 1.25 g. Water at 100° dissolves about .7 g. Hence a solution saturated at say 20° forms a precipitate when boiled.

The saturated solution of the hydroxid is called lime-water, which absorbs carbon dioxid and forms calcium carbonate. (See tests for carbon dioxid.) It reacts readily with acids, forming salts in the same way as the oxid.

Calcium hydroxid forms the basis of mortars. The lime from which it is made by slaking is generally impure, containing small amounts of silicon dioxid, sand, clay, and oxids of iron. In preparing and using the mortar, the first chemical change is produced when the lime is slaked according to the reaction already described. Enough water is added to the lime to complete the chemical change, and to form a thick, pasty mass. When sufficient water is added to this to form a thinner liquid, *i.e.* a mixture in which the hydroxid is suspended in the water, the product is called "milk of lime." (There are marked physical differences between the slaked lime made in this manner and that produced by the slow assumption of water. The latter product is a dry non-adhesive powder.)

The "slaked lime" is next thoroughly mixed with more or less sand (about one part of slaked lime to four parts of sand,

which must be angular and not rounded pieces). When the mortar is used, the first change is that of drying, and accordingly there is the deposition of the hydroxid often in crystals, which was held in solution by the water. This appears to cause the hydroxid to adhere closely to the rough grains of sand. But now the capacity of the hydroxid to absorb carbon dioxid comes into action, and there is slowly formed calcium carbonate, which hardens the whole mass. The sand gives a hard portion to the mortar, and undoubtedly facilitates the absorption of carbon dioxid by making the mortar somewhat porous. In nature, calcium carbonate often serves as a cement to hold the parts of rocks together. For example, the case of certain conglomerates and sandstones.

The so-called *hydraulic cements* have, as a basis, lime, and in addition about 30 per cent of sand and clay (see under CLAYS), of which 20 to 25 is the latter substance. Quite generally these constituents are artificially mixed and thoroughly ground together. The whole mass is now heated until the carbonate is decomposed and the water is driven off. When such a mixture is wet again and allowed to stand, chemical and physical changes occur that render the mass very hard. The process of hardening is probably due to the absorption of water and the union of the calcium oxid with sand and aluminium oxid under these conditions. The larger the amount of clay used, the more rapid is the hardening. The complete explanation of the changes has not been made.

Calcium hydroxid is also used in medicine and in many manufacturing processes, such as glass-making, in tanning, and in the production of the alkalis.

(*b*) **Salts of Calcium.** — The salts all correspond to calcium monoxid. The metal forms salts with all of the acids.

The principal salts of calcium are the chlorid, fluorid, hypochlorite, sulfate, phosphates, carbonates, and silicates.

Calcium Chlorid ($CaCl_2$); Crystals ($CaCl_2.6\,H_2O$). — Calcium

chlorid is produced as a waste substance in many manufacturing processes; for example, in the production of ammonia. It is a crystalline compound, but readily absorbs water from the air in sufficient quantity to dissolve the solid. It is often used, after being made anhydrous, to dry gases, and as a desiccating agent generally. When the crystallized salt is heated to 200°, four of the molecules of water escape. Above 200° the salt fuses, and at about 450° loses the remaining two molecules of water. When the anhydrous salt absorbs water, heat is given out; but when the crystals of the chlorid are dissolved, heat is required. Starting at a temperature of about 0°, a temperature of $-48°$ can be produced. The dry salt absorbs ammonia forming a compound having the formula $CaCl_2.8\,NH_3$.

Calcium Fluorid (CaF_2). — Calcium fluorid presents the peculiarity among the halogen salts of this base of being insoluble in water. It is found in nature quite widely distributed. The mineral is known as fluorspar. It is usually crystallized in cubes, although it is found sometimes in octahedrons. (See page 43, Part I.) It is a very stable compound, as is shown by its use as a flux, since under these conditions it is not decomposed by heat nor by the substances with which it is fused. The fluorid is the source of hydrogen fluorid (HF). The other halogen salts resemble the chlorid in their properties.

Calcium Hypochlorite ($Ca(ClO)_2$). — Like all the salts of this acid (hypochlorous), this compound is very unstable, yet on this fact depends its usefulness. It is a convenient means of storing the disagreeable but indispensable agent, chlorin. The compound is prepared by passing chlorin gas over slightly moistened calcium hydroxid (slaked lime). The reaction that occurs is one about which there is some disagreement among chemists, but it is probably thus: —

$$Ca(OH)_2 + Cl_2 = Ca\begin{cases} O-Cl \\ Cl \end{cases} + H_2O.$$

The reaction commonly represented as occurring under these conditions was determined from analogy to be

$$2\,Ca(OH)_2 + 2\,Cl_2 = Ca\begin{matrix}\diagup O-Cl \\ \diagdown O-Cl\end{matrix} + CaCl_2 + 2\,H_2O.$$

It was known that chlorin produced a similar result when it acted on sodium or potassium hydroxid. Thus: —

$$2\,NaOH + Cl_2 = Na - O - Cl + NaCl + H_2O.$$

Some of the reasons for supposing that an action occurs similar to that just given are: —

(*a*) That no calcium chlorid (or very small quantities of it) is present in bleaching-powder. Calcium chlorid is a very deliquescent salt, and according to this reaction it constitutes over .4 of the product. The product, therefore, should be very deliquescent. It is only slightly so.

(*b*) Alcohol readily dissolves calcium chlorid, but when bleaching-powder is treated with this solvent, only a very small amount of the salt is found to be dissolved.

(*c*) When the dry bleaching-powder is treated with carbon dioxid for a sufficiently long time, all of the chlorin of the powder is set free. It is a well-known fact that carbon dioxid cannot decompose calcium chlorid.

Whenever the bleaching-powder is treated with water, there is calcium hypochlorite ($Ca(ClO)_2$), calcium chlorid ($CaCl_2$) in solution, and a residue of calcium hydroxid ($Ca(OH)_2$). The reaction in reference to calcium chlor-hypochlorite is probably

$$2\,CaOCl_2 + H_2O = Ca(ClO)_2 + CaCl_2.$$

This reaction does not account for the calcium hydroxid always left as a residue when bleaching-powder is treated with water. It is probable that there is free calcium hydroxid left

when the powder is prepared in the usual manner. Prepared in the usual manner, the product contains, at most, but 35 to 40 per cent of available chlorin. This corresponds to about 2 molecules of chlorin and 3 molecules of the hydroxid, the per cent of each varying with the amount of impurities in the original hydroxid. The amount is also affected by the fact that a small amount of the chlorin is often combined as calcium chlorate ($Ca(ClO_3)_2$). The temperature at which the absorption occurs determines the amount of the chlorate that is formed. For example, at 50° the change to the chlorate is quite rapid. Suspended in water at 100°, the change in the calcium hydroxid just referred to takes place more readily, and the fact is made use of in preparing potassium chlorate. (See under POTASSIUM.)

The principal uses of the bleaching-powder are that of bleaching or rendering colorless organic coloring-matter, and that of an oxidizing and disinfecting agent. The chlorin is set free by any of the acids. The product in all cases, so far as the bleaching action is concerned, is free chlorin. The application of the agent in bleaching is best illustrated by an example. In bleaching brown cotton cloth, a dilute solution (about 2 per cent) of the bleaching-powder is made, and the cloth, properly cleaned, is wet with this solution. It is now placed in a dilute solution of such an acid as sulfuric or hydrochloric. The free chlorin attacks the coloring-matter of the fibre, which is less resistant to the destructive action of the agent than is the fibre itself, and thus destroys it without decomposing the latter. When the coloring-matter is destroyed, the further action of the chlorin on the cloth is stopped by washing it and immersing in a solution of such a substance as sodium sulfite. (See under SULFITES and under CHLORIN, Part I.)

The reaction of sulfuric acid with the bleaching-powder may be represented thus: —

$$2\,H_2SO_4 + Ca(ClO)_2 + CaCl_2 = 2\,CaSO_4 + 2\,HCl + 2\,HClO;$$
$$HClO + HCl = Cl_2 + H_2O.$$

Hydrogen chlorid decomposes bleaching-powder, setting chlorin free, and is itself also a source of chlorin under these conditions. This is due to the action of the nascent oxygen of the hypochlorite. The amount of chlorin is just double what the hypochlorite would yield.

$$Ca(ClO)_2 + 4\,HCl = 2\,Cl_2 + CaCl_2 + 2\,H_2O\,;$$
$$Ca(ClO)_2 + 2\,HCl = Cl_2 + CaCl_2 + O_2.$$

Bleaching-powder may also be a source of oxygen. At red heat the compound is decomposed, and oxygen escapes. Its action as an oxidizing agent and as a source of oxygen is illustrated by its action on cobaltous oxid. When a cobaltous compound, like the nitrate, is added to a solution of bleaching-powder, cobaltous oxid (CoO) becomes cobaltic oxid (Co_2O_3). But when this oxid is once formed, it appears to be attacked by the nascent oxygen from the hypochlorite, and it gives up one atom of its oxygen to form the molecule O_2, and the cobaltic oxid becomes cobaltous again, to be again in turn oxidized. This action continues as long as there is any bleaching-powder undecomposed. Thus a small amount of cobalt nitrate serves to set free an indefinite amount of oxygen, provided that the bleaching-powder is supplied for it to act upon. The reactions are as follows: —

$$3\,Ca(ClO)_2 + 12\,Co(NO_3)_2 = 2\,Co_2O_3 + 3\,CaCl_2 + 8\,Co(NO_3)_3\,;$$
$$Ca(ClO)_2 + 2\,Co_2O_3 = CaCl_2 + 4\,CoO + 2\,O_2\,;$$
$$Ca(ClO)_2 + 2\,CoO = CaCl_2 + 2\,Co_2O_3.$$

Other metallic oxids cause this compound to yield oxygen.

As a disinfectant, deodorizer, etc., its action is due to the chlorin set free from the calcium hypochlorite. It is, therefore, evident that it is practically necessary, if the agent is to be effectually used, that some acid or other decomposing agent that acts quite rapidly be employed. The carbon dioxid of

the air decomposes it so slowly that it is only slightly, if at all, effective.

Calcium Sulfate ($CaSO_4$); Crystals ($CaSO_4.2H_2O$). — Native calcium sulfate is quite abundant and widely distributed. It is found in a variety of forms and is known under several different names. The crystalline variety holding two molecules of water is called gypsum. A massive fine-grained variety of gypsum is known as alabaster. Gypsum is often found in nearly colorless, transparent crystals. This variety is called selenite. Much of the native gypsum is variously colored by iron and other compounds. Nature also furnishes a crystallized calcium sulfate that has no water of crystallization and is, therefore, called anhydrite.

Gypsum is quite readily decomposed at 120°, most of the water being driven off, and a nearly anhydrous sulfate is left behind. The substance, when ground to a fine powder, is known as plaster of Paris, and possesses properties that make it useful in many ways. Plaster of Paris is a white powder that takes up water corresponding in amount to that driven off from the gypsum in its preparation. The mass hardens and expands after absorbing the water and retains the form in which it "sets." It is therefore used in making casts and moulds of various objects, in stucco work, and in what is called "hard finish" on the ordinary plastered walls of houses. Lime and sand are often added to the "plaster of Paris" to prevent too rapid hardening, and at the same time the final dried product is harder. Plaster of Paris is used in many other ways; for example, in "staff," as a fertilizer, in cements, in giving body and finish to writing-paper, etc. If the gypsum is heated to 190°, it loses all of its water, and only slowly takes up water again, and is thus useless for most of its applications in the arts.

Calcium sulfate is partially soluble in water and in hydrochloric acid. At ordinary temperatures 1 g. of the sulfate

requires 400 g. of water for its solution. Its solubility is but slightly increased at 100° (1 g. to 450 g.). Owing to the wide distribution of gypsum it is often present in natural waters, giving to such waters what is called permanent hardness. (See CALCIUM CARBONATE.)

Calcium Phosphate ($Ca_3(PO_4)_2$). — Calcium phosphate is found in nature principally in the form of phosphorite and apatite. Phosphorite occurs in quite large masses in North Carolina and Florida and in many European localities. It is also a valuable constituent of guano. Apatite is the normal phosphate along with calcium fluorid ($CaF_2.3\,Ca_3(PO_4)_2$). Sometimes the chlorid takes the place of the fluorid. The normal calcium phosphate is also an essential constituent of animal bones, the ash of which contains about 85 per cent of this phosphate.

Normal calcium phosphate is practically insoluble in pure water, but it is dissolved by weak acids, and even waters charged with carbon dioxid decompose it. Under phosphorus in Part I. of this work the cycle of changes through which phosphorus passes in becoming a part of the animal body was pointed out, and it is only necessary here to emphasize some of the facts there mentioned. Owing to the ready solubility of the normal phosphate in weak acids, the rain water which is charged with carbon dioxid is able to slowly dissolve the compound for the use of plants. Finely ground bones are thus useful as fertilizing food material for plants. When stronger acids, like H_2SO_4, act upon the normal phosphate from bones or from the native phosphate, the salt is transposed, and a soluble acid salt is formed. The reaction is —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = 2\,CaSO_4 + CaH_4(PO_4)_2.$$

This acid salt is quite soluble, and therefore is useful plant food. It is, however, not necessary that the normal phosphate receive this treatment, as has been just pointed out.

The acid salt is much used in baking-powders to decompose sodium bicarbonate.

Calcium Carbonate ($CaCO_3$). — Calcium carbonate is the source of most of the other calcium compounds. Its abundance and distribution as limestone, marble, chalk, and calcite, or calc spar, have already been referred to under the topic of occurrence. Limestone is more or less impure calcium carbonate, which often constitutes a large proportion of the rock masses of the earth's crust. Marble is a crystalline and somewhat impure calcium carbonate. Some of the Italian marbles, like the Carrara marble, are very nearly pure calcium carbonate. Calc spar is the pure crystallized carbonate. Chalk is calcium carbonate which has constituted the shells of minute organisms which have become more or less compacted together.

Since calcium carbonate is insoluble, it can be prepared by precipitation; for example, it is formed by the action of ammonium carbonate on a soluble[1] calcium salt like the chlorid.

One litre of pure water dissolves 18 mg. of calcium carbonate, there being but little variability in the amount with varying temperatures. If, however, the water is saturated with carbon dioxid, about 3 g. are dissolved under the same conditions otherwise. Natural waters (see this topic in Part I.) coming in contact with limestone rock, therefore, often become saturated with the carbonate. Some infer that an acid carbonate is formed, $Ca(HCO_3)_2$, which is more soluble than the normal salt, corresponding with the acid sodium or potassium carbo-

[1] The term *soluble* is only a relative one, and there is no fixed limit beyond which a substance is considered insoluble, and up to which any substance is said to be soluble. There are very few salt compounds that are not to a certain degree soluble in water. The variability, for example, is all the way from soluble in equal parts to soluble one part in a million parts of the dissolving medium. Calcium chlorid is an example of one extreme, and calcium oxalate of the other. The words *partially* and *slightly* are sometimes used to give certain limits to solubility. Calcium sulfate is partially soluble in water.

nates (which see). Like these carbonates, the calcium salt is decomposed by heating, so that boiling the solution serves to precipitate all but the usual amount that the water will hold in solution, as just stated. The carbon dioxid is driven off. Slow evaporation produces a similar result. The capacity to form acid salts, or at least to form soluble salts in water containing dissolved carbon dioxid, is quite characteristic, in general, of the carbonates. Natural waters containing these dissolved carbonates are called "hard." This "hardness" is called temporary "hardness" to distinguish it from permanent hardness caused by calcium sulfate. Temporary "hardness" is largely destroyed by boiling the waters, when the deposition of the normal carbonate just pointed out occurs. This accounts for the "crusts" and scales that form in boilers and kettles when such waters are heated. The term *hardness* refers to the effect that "hard" waters have in producing insoluble organic salts with the base of the carbonates. Such carbonates produce insoluble salts with the organic salts which constitute soaps, and therefore use up a corresponding amount of soap. This solid matter adheres more or less closely to the fibre of the material which is being cleansed by the soap. When the water is boiled before using, nearly all of the carbonates are precipitated. Calcium and magnesium sulfates are not thus precipitated, and thus they impart to the water permanent hardness, since they produce the same precipitates as the corresponding carbonates. Soluble carbonates like those of sodium and potassium precipitate this excess of these acid salts and are thus said to soften the water. Sodium carbonate is commonly thus used under the name of "sal soda."

In general, the facts just given account for the formation of stalactites and stalagmites. How?

The uses of native calcium carbonate are numerous, to many of which attention has already been called. For example, its use as a flux in manufacturing pig iron was spoken of under

iron; for building-stone, and in the production of glass (see under GLASS).

Calcium Silicate ($CaSiO_3$); Glass. — Under the study of aluminium, the silicates were briefly noticed. The subject is one of too much complexity to be considered at length in an elementary treatise. The silicates are all insoluble in water except those of the alkalis and such of the complex silicates as contain the alkali bases. Such silicates are decomposed under the conditions that obtain in most soils. The complex silicates that contain the base calcium are also very slowly decomposed, especially if much carbon dioxid is present in the soil water. Calcium silicate forms a part of many of the polysilicates.

The simple silicates, corresponding to the acid (H_2SiO_3), are not widely distributed. Calcium silicate ($CaSiO_3$) is formed, and is known as meta-silicate or wollastonite. It is produced when silicon dioxid (SiO_2) is fused with calcium carbonate.

This compound is the basis of most of the different kinds of glass. It is, however, difficultly fusible, and there is added to it a certain amount of either sodium or potassium silicate, which are quite easily fused. These alkali silicates render a mixture with calcium silicate much more fusible. These fused mixtures are entirely colorless and transparent in moderately thin layers, provided the materials from which they are made are pure. The materials which are used for common glass are native quartz, calcium carbonate (sometimes lime), potassium or sodium carbonate, and sometimes sodium (or potassium) sulfate and carbon take the place of the alkali carbonates. The proportion of the ingredients varies somewhat with the kind of glass to be made, but for the more common glasses the proportions are fairly constant. The silicon dioxid is always in excess of the amount required to unite with the bases used. For example, in 100 kg. of the fusing mixture there is from 65 to 75 k. of sand and about equal amounts of each of the oxids of calcium and sodium (or potassium). A study of the following

reaction will show that if all the silicon dioxid becomes a part of the silicates, there should be very nearly as much of the bases as there is of the silicon dioxid.

$$2\,SiO_2 + CaO + Na_2O = CaSiO_3 + Na_2SiO_3.$$

Glass is therefore a homogeneous mixture of silicates holding in solution silicon dioxid. In some cases aluminium silicate is present in small amounts.

The properties of glass vary to quite an extent in accordance with its changes in composition, and the general classification of glasses is made on the basis of composition.

(*a*) Hard, crown, or Bohemian glass has potassium silicate in place of the sodium salt. It is quite hard, and is not readily attacked by the usual reagents, *i.e.* acids and alkalis. Its point of fusion is considerably higher than that of common glass. It is accordingly used for chemical apparatus, especially for combustion tubes and other apparatus that are to be heated to high temperatures. This glass is also known as potash glass.

(*b*) Soda glass (or soft glass) is prepared from the same ingredients, except that sodium carbonate (or sulfate and carbon) are used in place of the potassium carbonate. Such a glass is quite easily fused, and is used for tubing, window, and plate glass and for many other purposes in which the glass is not to be brought in contact with acids or alkalis. It is very slowly dissolved by water at 100°. Plate glass differs from ordinary window glass particularly in the method of its manufacture. Window glass is blown into cylinders, which are then cut, softened, and flattened out. The plate glass is a soda glass (and sometimes soda-potash glass) that is run into a flat mould. It is afterwards polished. Its thickness is more uniform than is that of window glass.

(*c*) Lead, crystal, or flint glass has lead silicate instead of calcium silicate along with potassium (sometimes sodium) silicate. The varieties of this glass depend on the variability

in the amount of lead silicate which it contains. The amount varies from 42 to 67 per cent. This glass is characterized by high refractive power, and is often used for lenses, and in general it is employed in optical instruments. It takes a very brilliant polish, has a bright lustre, and is therefore used for ornamental purposes. Such glass is very fusible.

When the amount of lead silicate in the glass reaches 60 or more per cent, it is called strass, and is used, after being cut and polished, in jewelry. Such jewels are often called "paste" diamonds.

(*d*) Another variety of glass, called bottle glass, differs from the soda glass only in the fact that quite impure materials are used in its preparation. Glass acts very much like borax in reference to the metallic oxids; that is, glass has present an excess of a weak acid oxid which unites under the conditions with the metallic oxids, in much the same way as borax has an excess of an acid oxid (B_2O_3), and at the temperature of fusion it unites with the metallic oxids. (See COBALT and NICKEL BEADS.) The silicates of iron (-ous), cobalt, copper, uranium, chromium, etc., are colored and impart their color tints to the glass. Iron (-ous) imparts a green color to the glass, while iron (-ic) colors it a light yellow, the depth depending, of course, on the quantity of the iron compound that is present. Manganese silicate colors glass a purple to violet. These facts are made use of in decolorizing glass that is colored green. Manganese dioxid (MnO_2) is added in small quantities to molten glass. This oxidizes a portion of the ferrous compound to the ferric condition, which only slightly colors the glass. The green color due to the unchanged ferrous silicate is neutralized by the violet manganese silicate, green and violet being complementary colors. These facts enable the glass-maker to use quite impure materials for making such glass as window and bottle glass.

When colored glass is desired, it is made according to the

facts previously stated, by using the proper metallic oxid. For example, red glass by using copper sub-oxid (Cu_2O), or by using a mixture of gold and tin oxids; green glass, by using cupric (CuO) or chromic oxid (Cr_2O_3); blue, by cobalt oxid (CoO); etc. Only very small amounts of these oxids are necessary to impart the desired tint.

All of the glasses are attacked by the alkalis, as is often illustrated by the "sticking" of the glass stoppers of bottles containing solutions of such substances. The acid silicon dioxid is converted into the alkali silicate, and the stopper becomes attached to the mouth of the bottle. Hydrogen fluorid also attacks all glass, owing to its affinity for the silicon. (See under FLUORIN, Part I.)

Glass is generally quite brittle, but is especially so if it is suddenly cooled. It appears to be under a state of tension held by an outside shell; for when this is broken, even by a scratch, the whole mass separates into a great number of pieces. This condition of the glass is avoided by slowly cooling it, or, as it is called, by annealing it.

Calcium Sulfid (CaS). — Normal calcium sulfid is soluble in water, and is not prepared in the "wet way." It is a yellowish white compound produced by reducing calcium sulfate by means of carbon. The salt is decomposed by much water forming hydrogen sulfid (H_2S) and calcium hydroxid ($Ca(OH)_2$).

This sulfid, like those of barium and strontium, is phosphorescent. They are used (especially the CaS) under the name of *luminous paint*, since, when they have been exposed to light for quite a period, they continue to give out light when placed in the dark. The emission of light ceases in a comparatively short time. These facts make the paint useful in painting clock faces, the walls of passage ways in buildings, keyholes, plates, etc. Calcium unites with sulfur in several proportions. This is also a characteristic of the alkaline bases. Calcium quinqui-sulfid (CaS_5) is the best known of these com-

pounds. When these sulfids are treated with an acid, they are decomposed, and sulfur in a finely divided condition is set free. The calcium salt of the acid used and hydrogen sulfid are also formed.

BARIUM.

Occurrence and Distribution. — Barium is much less widely distributed in nature than calcium. The element occurs principally in two minerals known as heavy spar, barium sulfate ($BaSO_4$), and witherite, barium carbonate ($BaCO_3$). Barium forms a part of several rare minerals. Witherite is found in England in workable quantities, and heavy spar is mined in Virginia, Connecticut, and Massachusetts.

Preparation. — The sources of barium and its compounds are the two minerals heavy spar and witherite. The element is most readily obtained from witherite. This is decomposed by hydrochloric acid, and from the chlorid thus formed the metal is separated by the methods given for the preparation of calcium. (See CALCIUM.)

Properties. — Barium has the same general physical and chemical properties as the metal calcium. Its chemical properties are simply more intense. For example, it decomposes water more energetically than calcium does, or in other words it is more strongly basic than is calcium or strontium. It melts at a temperature below red heat. Its specific gravity is 3.75.

Name and History. — The element was named barium by Davy in 1808. The name, which means heavy, had been applied to several of its compounds because of their high specific gravity. Heavy spar, or barite, is an application of this name to a mineral containing barium.

Atomic Mass and Valence. — Barium forms no volatile compounds, and its specific heat has not been determined. Hence

the atomic mass, determined by these processes, cannot be used to correct the results of quantitative analysis. Barium replaces two atoms of hydrogen in forming salts. If the amount equivalent to two atoms of hydrogen is assumed to be an atom, then the atomic mass is 137. It is certainly this number or some multiple of it. This is the amount of barium that unites with two atoms of chlorin.

Since the element replaces two atoms of hydrogen, it is bivalent.

Experimental Study, No. 34.—(*a*) Treat 5 to 10 g. of witherite, or the artificial barium carbonate, with dilute HCl, and heat until it is all dissolved. What gas escapes? Write the reaction, remembering that barium is bivalent. Evaporate to dryness, redissolve in a little water, and allow the salt to crystallize.

(*b*) Make the usual study of a solution of the salt just prepared, using the usual reagents. All precipitates are the normal salts. Note that $K_2Cr_2O_7$ forms the normal chromate instead of the acid salt.

(*c*) Add a saturated solution of $CaSO_4$ to a solution of a barium salt, warm, and allow to stand a few minutes. Note the time of precipitation. Which is the more soluble, $CaSO_4$ or $BaSO_4$? What is the solubility of the sulfates studied thus far? Note the solubility in acetic acid of barium oxalate.

(*d*) Make the platinum wire test as was done in (*f*) in the study of calcium compounds. The result is characteristic for barium compounds.

(*e*) Make a mixture containing carbon, barium sulfate, and sufficient oil to make a thick paste. (Say 5 g. or less of finely powdered sulfate and 2 g. of carbon.) Place this mixture in a covered porcelain (or platinum) crucible, and heat to red heat until the oil is decomposed and the action is complete. When cool, examine the residue. The oil is rich in the element carbon; what is its use therefore? What was the effect of the heat on the oil? If necessary, heat some oil alone,

away from the air, *i.e.* in a closed crucible. Remove some of the residue, placing it in a test-tube, and add HCl. Warm. What gas escapes? What is the source of the sulfur? Filter the acid solution, neutralize with ammonium hydroxid, and add $K_2Cr_2O_7$. What does the result show? How is the barium combined in the fused residue? What would have been the result had other sulfates been used? Where is the oxygen of the sulfate?

(*f*) Place 2 to 5 g. of barium nitrate in a crucible, and heat to complete decomposition. What gases escape? Judging from the effect of heat on nitrates, what is the residue? When the mass has cooled, remove it from the crucible and add 2 or 3 cc. of water. (Or add the water to the mass in the crucible.) Note and explain any changes in temperature after adding the water. Compare with action of water on CaO.

(*g*) Heat some barium dioxid to red heat. What gas escapes?

Review the preparation of hydrogen dioxid.

Compounds of Barium.

(*a*) **Oxids and Hydroxids.** — Barium, as has been seen, rapidly oxidizes in the air, but the oxid is usually made by decomposition of the nitrate at red heat. It is a solid gray-colored substance that reacts with water, the reaction being accompanied by much heat. Barium hydroxid is formed by this action. The hydroxid is a soluble white crystalline substance markedly basic, and forms salts with all acids. It rapidly absorbs carbon dioxid, and is often used for this purpose. Its water solution is caustic, and the hydroxid is often called caustic baryta to distinguish it from the other caustic alkalis. It is a very stable compound, and is not decomposed at red heat. (Compare with other hydroxids in reference to the action of heat.) The compound has several industrial and scientific applications.

For example, it often takes the place of calcium hydroxid in sugar-refining. It is used to absorb carbon dioxid in analytical chemistry.

Barium oxid, when heated to a low red heat in the presence of oxygen or in the air, absorbs an atom of oxygen and becomes BaO_2, barium dioxid, or peroxid. When the dioxid is heated to full redness, it is decomposed, oxygen is set free, and barium oxid is left as a solid residue. Advantage is taken of these facts to procure oxygen from the air. The air, freed from carbon dioxid, is passed over barium oxid placed in a tube which is heated to dull redness. When the absorption is complete, the tube is heated to full redness, this oxygen is given off, and the oxid, when cooled, is ready to absorb more oxygen. By the proper arrangement of apparatus, the process is quite effectual in producing this useful gas. An interesting fact in reference to this process is, that after the oxid has been used a few times, it loses, to a great degree, its capacity to absorb oxygen, and must be regenerated before further use. This may be done by converting it into the carbonate or nitrate, and decomposing this product.

It has been discovered recently that the conditions of variability of temperature which determine the absorption and giving off of the oxygen by barium dioxid, in the process just described, may be replaced by a variability of pressure and with more satisfactory results. The barium oxid is placed in the proper apparatus, heated, and air forced in, under considerable pressure, until the oxid is saturated. The nitrogen is now forced out, the vessel closed, and the space exhausted by gas pumps, when the oxygen is set free and pumped into the proper receiver. The process is now repeated from the beginning, and so on continuously. The use of the dioxid as a source of hydrogen dioxid has been referred to in Part I. under that subject.

(*b*) **Salts.** — Barium, as has been seen, is strongly basic,

and therefore forms salts with all of the acids. Most of these compounds are of interest from the chemical standpoint only. They all contain barium in the bivalent condition, and have many of the general properties of the corresponding salts of calcium. They are usually prepared from the minerals witherite and barite. They are prepared from witherite with the least difficulty, and it is consequently the source of the compounds when the mineral can be had for this purpose.

The general method of preparation from the sulfate or barite has been given in (*f*) of the last study. These salts are poisonous. Barium compounds, especially those that are easily decomposed, color the Bunsen flame a light green.

The principal salts are the chlorid ($BaCl_2.2\,H_2O$), barium nitrate ($Ba(NO_3)_2$), barium carbonate ($BaCO_3$), barium sulfate ($BaSO_4$), and barium chlorate ($Ba(ClO_3)_2$.

Barium chlorid is a crystalline compound soluble in pure water, but is precipitated unchanged from solution by hydrogen chlorid. It is used as a reagent for recognizing the sulfates or free sulfuric acid. All the other salts of barium are soluble in hydrochloric or nitric acids except barium fluo-silicate ($BaSiF_6$). Hence in the absence of this acid, or its soluble salts, the reagents definitely determine the presence of sulfates in solution.

Crystallized barium chlorid ($BaCl_2.2\,H_2O$) is decomposed at 114°. The water wholly escapes at this temperature, leaving a white powder of pure chlorid ($BaCl_2$). By continued red heat in the air, the compound slowly decomposes.

Barium nitrate and *chlorate* are used in fireworks, or in pyrotechny, to produce the green "fires." There is always present in the mixture used for this purpose some substance that is readily oxidized to aid in the decomposition of the compounds, and to produce the high temperature necessary for the flame. Such substances as carbon, sulfur, sulfids, like Sb_2S_3, etc., are used.

Barium carbonate ($BaCO_3$) is of interest, since it is one of

the compounds of the element used in its separation and recognition.

Barium sulfate is one of the two very insoluble sulfates. It can be distinguished from lead sulfate by the fact that it readily dissolves in sulfuric acid (concentrated), while the former is only slightly soluble. The production of the lead globule when the lead sulfate is heated on charcoal is another means of distinction. The native sulfate is much used as a white pigment in painting. It does not blacken by exposure to the air, and, from this point of view, is superior to lead carbonate as white pigment.

STRONTIUM.

Occurrence. — Strontium, like barium and calcium, occurs in the minerals known as strontianite and celestite, the carbonate and sulfate. These minerals are quite rare, although the carbonate is found in quite large deposits in a few localities.

Preparation and Properties. — Strontium is prepared from the carbonate or sulfate. It is generally converted into the chlorid, and is prepared by electrolysis by the same method as is used in preparing calcium and barium.

Strontium possesses physical and chemical properties closely resembling those of calcium and barium. It stands between these two elements in reference to its chemical activity, and the descriptions given for calcium apply to this element with the limitation just referred to. Its specific gravity is 2.5, and its melting-point is higher than that of barium; namely, low red heat.

Name and History. — The discovery of this element is due to Sir H. Davy, although attention had been called to the probability of the existence of a new element in strontianite several years before its discovery. It was first prepared and

studied by Bunsen and Matthiessen in 1855. The element was named from a Scottish village, Strontian, where stronianite was discovered.

Atomic Mass and Valence. — The facts in reference to the determination of the atomic mass of strontium are like those connected with barium and calcium. The first study was made in 1816 by Stromeyer. Several examinations have been made since, all the results of which are substantially in agreement. Two atoms of chlorin were found to be equal to 87.3 parts of strontium. This is the exchange equivalent of strontium, and stands as its atomic mass. The element is bivalent, since it replaces two atoms of hydrogen in salts.

Experimental Study, No. 35. — Follow the directions given in the last study, using the solutions of the corresponding salts.

Compounds of Strontium.

What has been said of the compounds of barium may be said of those of strontium with few exceptions. Strontium chromate is fairly soluble in water, and therefore is not precipitated by the usual chromate reagents. The sulfate of strontium is more soluble than barium sulfate, but less soluble than calcium sulfate. Therefore, a saturated solution of calcium sulfate will slowly form a precipitate from solutions of strontium salts. Strontium oxalate, like that of barium oxalate (as precipitates), are soluble in acetic acid, while calcium oxalate is insoluble under these conditions.

Strontium compounds impart a bright red color to a Bunsen flame. The nitrate is used in producing red "fires." These "fires" are made on the same general principle as are the green "fires" referred to under barium.

MAGNESIUM.

Occurrence and Distribution. — Magnesium is the sixth element in abundance in the earth's crust. It is never found free, but occurs combined in magnesite ($MgCO_3$), in a large number of mineral silicates, such as meerschaum, serpentine, steatite; associated with calcium carbonate in dolomite; in natural waters as the sulfate and chlorid and carbonate. The sulfate and chlorid are also found deposited in masses as double salts. (See under SALTS.) Although it forms but a small part of plants, yet it is claimed that it is an essential element in a fertile soil. Its compounds form a small part of the animal body.

Preparation. — This element like the three preceding ones has great affinity for oxygen, and is, therefore, not easily prepared by the usual method; namely, of preparing the oxid (if nature does not furnish it ready formed) and then removing the oxygen from it by means of carbon. The method commonly employed for preparing this very useful metal consists in heating together to a bright red heat dry magnesium and sodium chlorids, fluor spar and sodium, six parts of the magnesium chlorid to one part each of the other substances of the mixture. The sodium reacts with the magnesium chlorid, the sodium uniting with the chlorin, and the magnesium is set free. The other substances of the mixture serve as a flux and aid in excluding the air from the metal. The mass is stirred, which causes the small particles of the metal to run together into a button at the bottom of the fusing-vessel.

The metal prepared in this manner is not pure, and is further purified by distillation. The pure metal can be prepared by the method used for calcium.

Experimental Study, No. 36. — The study of magnesium has been so thoroughly made in Part I. that it is not necessary to repeat the facts here. These facts should be reviewed here in order that the chemical character of the metal may be freshly

brought to mind. The metal should be compared with the three preceding elements.

It is advisable, however, that the hydrogen equivalent of magnesium be determined to aid in fixing its atomic mass. Use the method, and follow the directions described under zinc (*e*), Study No. 30. Use quite dilute HCl, and weigh about .35 g. of magnesium. (The acid must be dilute in order that the reaction may not be too rapid.) Answer the same questions as are given under (*e*), substituting magnesium for zinc.

Physical Properties. — Magnesium is one of the light metals, having a specific gravity of only 1.75. It has the general appearance of silver, and is capable of taking a bright polish. It is quite a ductile and malleable metal, that fuses at about 700° and distills at 1000°. Its specific heat is .25.

Chemical Properties.— Magnesium is a strongly basic element, although less so than the alkaline earths. In pure oxygen at ordinary temperatures, it is only slightly oxidized. (Compare with alkaline earths.) It is only slightly oxidized in the air, but at its fusing-point in air or in oxygen it oxidizes rapidly, the action being accompanied by great heat and a brilliant white light. It does not decompose water at ordinary temperatures, and if the metal is pure, the action at the boiling temperature is very slow. The ordinarily impure metal decomposes water slowly at 100°, forming the usual products, hydrogen and magnesium hydroxid. The metal has a marked affinity for the halogens, uniting readily with these elements when they are in the gaseous form. Perhaps its most characteristic property is its great affinity for oxygen at high temperatures. When it unites with oxygen, the atomic proportions produce about 140,000 calories of heat. It therefore decomposes such oxids as carbon dioxid, sulfur dioxid, etc. (See studies in Part I.) It also removes the oxygen from many metallic oxids, such as lead, silver, and copper oxids. The metal dissolves readily

in nearly all acids, forming the salts of the acids and hydrogen.

Name and History. — The names *magnesium* and *manganese* were used interchangeably for some time, but were finally applied as explained under MANGANESE (which see). The magnesium alba of the early chemists was magnesium carbonate. It was shown to contain a substance which was distinct from lime as early as 1755. In the memorable year 1808 Sir H. Davy showed that this latter substance contained a new metal, — magnesium. The pure metal was not prepared, however, until 1852, when Matthiessen and Bunsen prepared it by electrolysis.

Atomic Mass and Valence. — The last study has shown that one part of hydrogen is equal to twelve parts of magnesium. This is, therefore, its atomic mass, or the latter is some multiple of this number. A study has been made of the sulfate of magnesium, and it has been found that the magnesium does not divide the hydrogen of sulfuric acid under any conditions when the sulfur and oxygen are in the proportion 32 : 64. This number, 24, is twice the hydrogen equivalent, but is accepted as its atomic mass. The valence is, therefore, 2.

Uses. — Magnesium has no wide applications corresponding to those of iron, copper, and many other metals, but it is quite extensively used because of its chemical properties, and especially because of the brilliant light produced by its oxidation. As has been shown, the heat of formation of magnesium oxid is about 140,000 calories. This great heat volatilizes portions of the metal, which are thrown outward before they are oxidized, and thus produce a flame consisting in part of white hot particles of magnesium. Then the oxid is an infusible solid, which therefore glows with a brilliant light because of the intense heat of oxidation. By the proper arrangement of apparatus, the magnesium can be supplied as fast as oxidized, and hence a continuous and brilliant light can be produced.

It is thus used in lighthouses and in projection lanterns. In the powdered form, it is used as a flash light for signalling. The light is rich in actinic rays, and it thus serves for producing light for photographing.

Experimental Study, No. 37. — (*a*) Prepare magnesium oxid from the metal, and examine its solubility in water and acids. Test the water in which some of the oxid has been boiled for alkalinity. Explain the changes, and write the reactions.

(*b*) Make the usual study of the action of table reagents, using the solution made by dissolving magnesium in HCl in the last study, or a solution of the chlorid or sulfate. Note the action of ammonium carbonate. (K_2CO_3) precipitates a basic carbonate of variable composition, $MgCO_3.n(Mg(OH)_2)$.

(*c*) To a solution of a magnesium salt add KOH. Compare with the alkaline earths. What is true of the solubility of the other hydroxids? How does the action of ammonium hydroxid differ from that of the fixed alkalis? Next add NH_4OH and NH_4Cl to the solution of the magnesium salt, and follow by KOH. Treat another portion of the solution in the same manner, using ammonium carbonate instead of KOH. These reactions are similar to several others that have been studied, in that there are formed soluble double salts with the reagent and the insoluble compound that is formed at first. They are as follows: —

$$MgCl_2 + 2\ KOH = Mg(OH)_2 + 2\ KCl;$$
$$2\ MgCl_2 + 2\ NH_4OH = Mg(OH)_2 + MgCl_2(NH_4Cl)_2;$$
$$Mg(OH)_2 + 4\ NH_4Cl = MgCl_2(NH_4Cl)_2 + 2\ NH_4OH;$$
$$MgCl_2 + 2(NH_4)_2CO_3 = MgCO_3(NH_4)_2CO_3 + 2\ NH_4Cl.$$

(*d*) To the solution of a magnesium salt add the two reagents NH_4OH and NH_4Cl, and then add Na_2HPO_4 or NH_4NaHPO_4. Note the way the precipitate is formed. Stir with a glass rod,

rubbing the latter against the sides of the vessel. This precipitation is quite characteristic for magnesium in the absence of other bases.

Compounds of Magnesium.

(*a*) **Oxid and Hydroxid.** — Magnesium oxid (MgO) is a white, bulky, amorphous powder, commonly known as magnesia. Under this latter name it has been used for a long time in medicine for many purposes. The oxid is less soluble in water than are those of the alkaline earths. One gramme of the oxid requires about 55,000 g. of water for its solution. However, enough is dissolved to produce an alkaline reaction. The oxid is commonly prepared by the ignition of the carbonate, which decomposes at 170°, thus showing the relatively weak basic character of this metal. (Compare with carbonate of alkalis and alkaline earths.) Yet the oxid, like those of the alkaline metals generally, will decompose ammonium salts, such as ammonium chlorid, setting ammonia free and forming a double salt. (See a similar reaction on page 299.) It is also prepared by the usual methods for producing oxids. The oxid is found in small quantities in nature in the mineral periclase.

The solubility just given for magnesium oxid is practically that of the hydroxid, since this is the product formed by the solution. This is one of the products formed when water is decomposed by magnesium, and its insolubility undoubtedly prevents anything but a slow action, as the hydroxid adheres to the metal, and thus prevents the water from coming in contact with it. Magnesium oxid moistened with water and permitted to stand for some time gradually hardens, probably owing to the formation of the hydroxid which under the conditions cements the whole together. It is for this reason added to cement. The mineral brucite is magnesium hydroxid.

(*b*) **Salts of Magnesium.** — The salts of magnesium, when soluble, are readily formed by the action of the acids on

either the metal, its oxid, hydroxid, or carbonate. The insoluble salts, like the carbonate, are formed by precipitation. With weak acids it forms basic salts, but has but little tendency to do so with the stronger acids. One of the marked peculiarities of magnesium is its capacity to form double salts, especially with ammonium and the alkali bases. The soluble salts are usually colorless and quite bitter to the taste.

Magnesium Chlorid ($MgCl_2$); Crystals ($MgCl_2.6\,H_2O$).— Magnesium chlorid is a very deliquescent salt, resembling its analogous compounds, the chlorids of calcium and strontium. The mineral carnallite is a double salt of magnesium and potassium chlorid ($MgCl_2.KCl.6\,H_2O$). This substance is found in quite large deposits at Stassfurt. The chlorid also forms crystalline double salts with sodium and ammonium chlorid of the same general composition. When the crystallized salt (normal) is heated sufficiently to drive off the six molecules of water, there is a mutual decomposition of the two molecules, and hydrogen chlorid escapes, and magnesium oxid is left as a residue. This decomposition takes place in a water solution of the chlorid if it is heated under high pressure; for example, such as is commonly produced in steam boilers. Natural waters sometimes contain this salt in solution, and when they are used in steam boilers, the solution becomes concentrated, in course of time, and the decomposition just spoken of occurs. The acid thus set free attacks the iron of the boiler and rapidly corrodes it. In the presence of sodium carbonate the acid is neutralized. Salts that readily form double salts with the chlorid also prevent this decomposition: such salts as sodium or potassium chlorid are examples. The double salts of magnesium and ammonium have been noted under the last study. The ammonium double salt is sufficiently stable to be separated by evaporation of its solution, but heat, 460°, readily decomposes them into the two original salts. The magnesium chlorid can be distilled unchanged at 708°.

Magnesium Sulfate ($MgSO_4$); Crystals ($MgSO_4.7\,H_2O$). — This salt of magnesium is widely distributed in nature in natural waters and in mineral deposits known as kieserite ($MgSO_4.H_2O$). This salt corresponds in composition to the substance left when the crystals of the sulfate are heated for some time to a temperature of 150°; *i.e.* at the temperature of 150° all of the water of crystallization is driven off except one molecule. To remove the last molecule requires a temperature of 220°. Magnesium sulfate forms double salts similar to those of the chlorid; *e.g.* $K_2SO_4.MgSO_4.6\,H_2O$.

Magnesium sulfate is used in medicine under the name of Epsom salts, since it was first noticed in the saline springs of Epsom, England. It is a purgative, and is often used in veterinary medicine for this purpose. It is also used in dyeing cotton goods and in giving weight to the same. The salt is very soluble in water, 1 g. requiring only about 4 g. of water for complete solution at ordinary temperatures. The sulfate is prepared for commercial purposes from the native deposits of kieserite.

Magnesium Carbonate. — Magnesium carbonate is one of the insoluble salts of this metal, and is therefore produced by precipitation. The precipitated compound is basic and of variable composition, depending on the conditions under which it is produced. One of these carbonates, known as magnesia alba, has the composition represented by the following formula: $3\,MgCO_3.Mg(OH)_2.3\,H_2O$. This compound is formed by adding sodium carbonate to a hot solution of magnesium sulfate. Heat readily decomposes this compound, leaving magnesium oxid (MgO). The normal carbonate, magnesite, is found in nature, and can be prepared by imitating the natural process. This carbonate, like most others, is insoluble in pure water, but also, like other insoluble carbonates, it is soluble in water saturated with carbon dioxid. If, therefore, the magnesia alba be suspended in water through which carbon dioxid is passing it dissolves, and the clear solution on evaporating at ordinary tempera-

tures, deposits crystals having the composition $MgCO_3.3\ H_2O$. If, however, the solution be kept hot and at the same time saturated with carbon dioxid, crystals are formed which have the composition of the normal carbonate ($MgCO_3$). The tendency of magnesium to form an hydroxid is seen when such a solution is evaporated at a raised temperature, for the original basic carbonate is left as a residue. The carbonate is found in natural waters that come in contact with dolomite, or magnesium and calcium carbonate united. Dolomite is widely distributed, and occurs in large masses. When such waters are heated, the carbonate is deposited, acting like calcium carbonate.

Other Salts of Magnesium. — Magnesium phosphate and especially magnesium ammonium phosphate ($MgNH_4PO_4$) are of interest because of their connection with analytical chemistry. When a solution of a magnesium salt is treated with ammonium chlorid (or other ammonium salt), the whole made alkaline with ammonium hydroxid, and a soluble phosphate is added, a crystalline precipitate is produced that is characteristic of magnesium. The precipitate is magnesium ammonium phosphate ($MgNH_4PO_4$), and is quite insoluble in water, 1 g. of the salt requiring about 45,000 g. of water for its solution if free ammonia is present. It is easily seen that this test might be reversed; *i.e.* it can be used to prove the presence of soluble phosphates in a given solution. (See tests for phosphoric acid, Part I., page 265.) This salt is decomposed by heat forming the magnesium pyro-phosphate (MgP_2O_7). (See Part I., page 267; also under test of arsenates).

Magnesium is the basic element in many native silicates. For example, talc, steatite, asbestos, olivin, serpentine, are the more common of these minerals. These silicates, like all the native compounds, are either salts of the normal or metasilicic, acids (H_4SiO_4 or H_2SiO_3), or they are poly-acid derivatives of these acids. Olivin is the normal silicate (Mg_2SiO_4). Serpentine is $(MgO)_3(SiO_2)_2.2\ H_2O$, and occurs in large masses, and is used

as a building-stone; talc has the composition represented by the formula $(MgO)_6(SiO_2)_5 . 2\,H_2O$; asbestos is a silicate of calcium and magnesium, and is noted for its infusibility and its low heat-conducting power. It occurs in fibrous masses, the fibres being sufficiently tough to permit them to be woven into cloth. It is used as a packing to prevent loss of heat and in various other ways in which the properties of indestructibility and non-conductibility of heat are useful.

Magnesium does not form a sulfid in the wet way, but it may be formed by reducing the sulfate with carbon, or by heating together magnesium and an excess of sulfur.

Experimental Study, No. 38. — (*a*) Prepare a solution containing the salts (chlorids) of barium, calcium, strontium, and magnesium. Suppose the solution is treated with NH_4Cl and NH_4OH, and then with $(NH_4)_2CO_3$, which bases are precipitated? In what combination? Filter out the precipitate and preserve the filtrate, No. 1. Wash the precipitate once, and add warm dilute acetic acid to it while on the filter paper. Warm again, and repeat the process if necessary to dissolve it all. In what combination are the bases now? Suppose this solution is treated with $K_2Cr_2O_7$, what bases are acted upon? What ones are in solution? Filter, and add to the filtrate NH_4OH, and then $(NH_4)_2CO_3$. Wash the precipitate until colorless, and dissolve in acetic acid; what bases are in solution, and how can they be recognized? Suppose K_2SO_4 or $(NH_4)_2SO_4$ are added, what is the precipitate? Suppose to this filtrate $(NH_4)_2C_2O_4$ is added, what may be determined by the result? Determine the presence of the base in filtrate No. 1.

(*b*) Suppose KOH be added to the fairly dilute solution directed in (*a*), of what does the precipitate consist? Again, suppose NH_4OH or $(NH_4)_2CO_3$ had been used, answer the same question. Same question for K_2SO_4.

THE ALKALI METALS.

The alkalis are sometimes designated for convenience, the fixed and the volatile alkalis. Under this term *alkali* is included sodium and potassium, lithium, rubidium, and cesium (the fixed alkalis), and ammonium (NH_4), the volatile alkali. The word *alkali* signifies "the ash," and is derived from the Arabic *al* and *kali*, which has the literal meaning just given. Sodium and potassium are the most important and abundant of these elements. These elements are about equally abundant in nature, standing, however, 7 and 8 in the scale representing the abundance of the elements. Sodium constitutes 20 parts of the earth's crust when oxygen is 480; calcium, 30. (For the relations of the alkali metals to each other, see under periodic system of classification.)

POTASSIUM.

See Part I., page 96, for the usual topics, except that of preparation, and compounds of.

Preparation. — Potassium stands at the head of the metals measured by basic character if the rare elements cesium and rubidium are excepted. It is readily inferred, then, that the preparation of the metal would involve considerable difficulty and the expenditure of much energy. The two marked affinities of potassium (and sodium) are for the halogens and for oxygen. For example, the heat of formation of potassium chlorid is 104,300 calories, and about the same for the oxid. Accordingly, this amount of energy must be used to set the element free from these combinations.

The element is commonly prepared from the carbonate K_2CO_3, by the action of carbon at white heat. The carbon must be in a very finely divided condition, and must be inti-

mately mixed with the carbonate. This condition is often produced by decomposing a potassium salt of an organic acid. Nature furnishes such a compound in the tartar of the grape. This compound has the formula $KHC_4H_4O_6$. When heated away from the air, the tartar is decomposed, forming K_2CO_3, carbon, and water principally. The residue, therefore, is the intimate mixture desired. This is transferred to a proper vessel and heated to a white heat. Under these conditions, carbon monoxid and potassium are formed, and both are in a gaseous state. The metal is cooled and placed in a liquid that contains no oxygen, like petroleum.

Potassium can also be obtained by electrolysis.

Compounds of Potassium.

(*a*) **Oxid and Hydroxid.** — From what has been already said, it is readily seen that the oxid can be formed from the two elements, oxygen and potassium, the formation being accompanied by a large amount of heat and light. It is also prepared by heating the hydroxid with potassium. It will be remembered that potassium sets one-half of the hydrogen of water free, forming potassium hydroxid. If, now, potassium is added to the fused hydroxid, as much more hydrogen is set free, and the oxid (K_2O) is left. The large amount of heat required to bring about this change is given out again when the oxid is brought in contact with water, the hydroxid being again formed.

When potassium is oxidized in the air, two oxids are formed, the one just mentioned, and one corresponding to the dioxid of the alkaline earths. It is represented by the formula KO_2, or by $KO_2—O_2K$. It is quite stable, but it is broken up by heat, by contact with water, or by fusing it with potassium. White heat is necessary to decompose it; the normal oxid (K_2O) and free oxygen are produced. It is a powerful oxidizing agent.

Potassium hydroxid is a commercial article, and is, consequently, made by the process that is the least costly. It is prepared from the carbonate (which see) by the action of calcium hydroxid. The reaction is readily understood when it is known that calcium carbonate is insoluble. A fairly concentrated solution of potassium carbonate (1 to 10) is boiled, and slaked lime is added until the carbonate is completely decomposed. The clear solution is evaporated to dryness, and the residue heated to fusion, when it is cast into sticks, or cooled in thin sheets, which are then broken up.

Potassium hydroxid is a powerful base, neutralizing all acids, forming the corresponding salts. It rapidly corrodes animal tissue, and is consequently often called caustic "potash," to distinguish it from "potash," or the crude potassium carbonate. It is a deliquescent substance, very soluble in water; so soluble that a solution saturated at ordinary temperatures contains about 50 per cent of KOH. Its affinity for carbon dioxid has already been noticed. It has many applications in the arts; *e.g.* in making soft soap, as a detergent, for drying gases, in the absorption of carbon dioxid, as a cautery, and in the preparation of other substances.

(*b*) **Salts of Potassium.** — The number of salts of potassium is as large as is that of the acids. These salts are, in general, all soluble in water, although there are several that are only partially soluble. In all of the salts potassium is univalent.

Potassium Chlorid, KCl. — Potassium chlorid is found in nature at Stassfurt, Germany, in the minerals carnallite ($KCl.MgCl_2.6H_2O$) and sylvite (KCl). Carnallite is the principal source of the chlorid and the other salts of potassium. Since potassium is essential to the growth and development of plants, this native salt becomes of great importance and value as a source of the potassium compounds that are used as a necessary component of a perfect fertilizer. Practically, all virgin soils contain potassium compounds in sufficient quantities to

meet the demands of the growing plant, but, in course of time, these compounds are nearly all removed by the ordinary methods of agriculture.

The origin of these soluble salts of potassium from rock disintegration has already been pointed out in the study of the origin of clays. It has been found that the soil retains to a great extent these compounds of potassium, while permitting salts of sodium, calcium, etc., to be slowly carried away by the soil water, and finally to reach the ocean and other large bodies of water. Sea-water, therefore, contains much more of sodium compounds than it does of potassium, although the amounts of each element in the original undecomposed rock of the earth's crust are about equal. Sea-plants require sodium compounds, the ash of which was formerly a source of sodium carbonate. (See under SODIUM.)

Potassium chlorid crystallizes in cubes which are soluble in three parts of water.

The Other Halogen Salts of Potassium. — These salts may be prepared by the usual methods, but they can be produced more cheaply by using the free elements and potassium hydroxid instead of the corresponding unstable acids. The halogens produce similar compounds when acting on any of the basic hydroxids. (See action of chlorin on calcium hydroxid.) When bromin or iodin acts on a hot potassium (or sodium) hydroxid, the following reaction occurs (using bromin as an example) : —

$$6\,KHO + 6\,Br = 5\,KBr + KBrO_3 + 3\,H_2O.$$

The bromin is added as long as it is absorbed. The solution is now evaporated to dryness and ignited, when the bromate is decomposed. (Compare with the chlorate.) Carbon is mixed with the iodate usually before ignition, since it is not so easily decomposed as the bromate or chlorate. The latter reaction is, —

$$2\,KIO_3 + 3\,C = 3\,CO_2 + 2\,KI.$$

Both these salts crystallize without water of crystallization in the form of cubes. They are very soluble in water. Potassium iodid has the peculiar property of dissolving iodin in such quantity that 166 parts (or molecules) of the salt dissolves 254 parts of iodin; *i.e.* the compound KI_3 is formed. It has been separated out by evaporating the concentrated solution over sulfuric acid. It gives up two-thirds of its iodin at 100°.

The iodid and bromid are valuable compounds in medicine and in photography.

Potassium Chlorate ($KClO_3$). — This salt is prepared by the method just given for the preparation of the bromid. That is, according to the reaction, —

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

In this case the potassium chlorate, being quite insoluble in water, crystallizes out, leaving the chlorid in solution. (See Part I., page 287.) The compound is often prepared, using calcium hydroxid instead of the comparatively costly potassium hydroxid, the potassium being furnished by potassium chlorid. Recalling the reactions produced in preparing bleaching-powder, it was seen that when the calcium hypochlorite solution was boiled, the compound was changed to the chlorate. If potassium chlorid is present (or is added afterwards), the potassium and calcium exchange places, owing to the low solubility of the chlorate and the strong basic character of the potassium.

The salt crystallizes in shining tabular crystals which are quite insoluble in water; *i.e.* 100 cc. of water will dissolve but 3.3 g. of the salt at 0°, and 6 g. at ordinary temperatures. It is much more soluble in water at 100°; namely, 60 g. in 100 cc. of water.

The most characteristic property of this compound — its oxidizing power — has been already noticed several times. (See Part I, pages 287, 288.) The uses of this substance are

dependent on this property, and the fact that it yields its oxygen at a relatively low temperature; namely, at 352°. For example, it is used in fireworks, in explosives, and in the production of matches.

The *common match* is an interesting article from the chemical standpoint. Before the year 1832, the starting of fires was a matter of considerable difficulty. The tinder box and flint was, at best, a slow process of igniting combustible material. The method given on page 288 (*c*), Part I., was also in use to a certain extent. Doebereiner's lamp was another device in use to a limited extent before this date. The essentials of a match are an easily combustible substance, which can ignite some less readily oxidizable substance, which may in turn ignite the material or fuel to be oxidized. Common phosphorus ignites at about 50°, a temperature that is readily produced by friction, and thus a comparatively high temperature is produced. If, therefore, some combustible material is at hand, a small amount of phosphorus will serve to ignite it. A substance like wood not only requires a high temperature for ignition, but it needs considerable heat energy to raise it to this temperature. The phosphorus alone oxidizes too quickly for this purpose. A mixture of sulfur and potassium chlorate, or of paraffine and the chlorate, is easily ignited, and burns with sufficient intensity to ignite wood. The mixture is made with glue or a similar substance which holds it to the wood. It is then covered with a thin coat of a brittle gum to keep the oxygen away from the phosphorus, but such that it is easily broken by friction. Many substances that are ready oxidizers may take the place of the potassium chlorate. Such oxidizers are manganese dioxid (MnO_2), red lead (Pb_3O_4), potassium chromate ($K_2Cr_2O_7$), and potassium nitrate (KNO_3). Such aids in carrying on the combustion as antimony sulfid (Sb_2S_3 or Sb_2S_5), lampblack, glue, gum, etc., are often employed instead of sulfur. Red phosphorus takes the place of the yellow phosphorus quite

generally in match-making now, since there is great danger to health in handling the common phosphorus, and comparatively little in using the red variety. The chlorate is also used in medicine.

Potassium Nitrate (KNO_3). — Potassium nitrate is constantly being formed in all fertile soils; but since it is soluble, it is, in part, carried away in the soil water, and also is in part used by the plants growing in the soil. It does not, therefore, accumulate in large quantities in such localities. However, in regions where but little moisture is present, such accumulations are formed by the process called nitrification. Saltpetre plantations are an imitation of nature's processes of nitrate formation. (See Part I., pages 244–246.) Since the discovery of the immense deposits of sodium nitrate on the west coast of South America, potassium nitrate has been produced by the action of potassium chlorid on this less valuable salt. The reaction depends on the fact that by a change of base, a less soluble salt can be produced (see page 24). For example, in the following represented reaction, —

$$NaNO_3 + KCl = KNO_3 + NaCl,$$

the sodium chlorid is less soluble than the potassium nitrate; and hence if the solutions are saturated, potassium nitrate will be separated out. A saturated solution of sodium nitrate at 100° (containing 180 parts of the salt) is treated with a like solution of potassium chlorid. The result depends on the facts that potassium nitrate is very soluble at 100°, and is comparatively insoluble at ordinary temperatures. One hundred grammes of water, when saturated with the nitrate at the boiling-point of this solution (116°), contains 335 g. of the nitrate; at 100° it dissolves 247 parts, while at ordinary temperatures the same amount of water holds only 30 g. of the salt. Sodium chlorid has about the same solubility in cold as in hot water. It is therefore readily understood that, under the conditions just given, the 180 parts

of sodium nitrate will form 214 parts of potassium nitrate, which, on cooling, will in part crystallize out.

This salt is quite a stable and crystalline compound that melts at 339° without decomposition. At higher temperatures it decomposes, giving off oxygen and leaving the solid potassium nitrite (KNO_2), and finally the oxid (K_2O). However, if some oxidizable substance is present under these conditions, it is readily oxidized, and the nitrogen is reduced. (See under MANGANESE, CHROMIUM, and the many other examples of this use.) The pure salt is not at all deliquescent, and is thus required, instead of the more common and cheaper sodium nitrate, in the manufacture of gunpowder, its chief application outside of its use in the laboratory.

The substances required for *gunpowder*, in addition to the nitrate, are those that have great affinity for oxygen and at the same time produce gaseous products accompanied by a high temperature. These conditions are met in the substances carbon and sulfur.

The main function of the latter element is to prevent the formation of potassium carbonate. If the reaction be expressed by the following equation, the proportions of the components can be readily determined: —

$$\underset{\substack{32\\ 11.9 \text{ per cent.}}}{S} + \underset{\substack{36\\ 13.3 \text{ per cent.}}}{3C} + \underset{\substack{202\\ 74.8 \text{ per cent.}}}{2\,KNO_3} = \underset{28}{N_2} + \underset{132}{3\,CO_2} + \underset{110}{K_2S}.$$

According to this reaction 1 g. of gunpowder will produce about 330 cc. of gas measured at 0°. (In practice it is about 280 cc. of gas.)

Under the influence of the temperature produced by the reaction it has been calculated that 1 cc. of gunpowder (about 1 g.) will produce about 2300 cc. of gas at temperature produced by the reaction. This means, of course, that the gas is

under one atmosphere of pressure, and that the reaction was practically instantaneous.

When the gaseous products of explosion are confined in a volume equal to that occupied by the powder before the reaction, the pressure developed is very great, and is variously stated to be from 15 to about 40 tons per square inch. The chemical action in gunpowder begins at about 300°, and may be produced by any means that will produce this temperature in any portion of the mass of powder. The rate of chemical change depends to a great extent, other conditions being the same, on the compactness of the powder and the thoroughness and care used in mixing the ingredients. The products of the ignition of the gunpowder vary somewhat from those indicated in the reaction just given. The details of these differences, however, do not belong to an elementary work.

Potassium Carbonate (K_2CO_3); Crystals ($2\,K_2CO_3.3\,H_2O$).— In speaking of the relation of potassium to plant growth, it was shown that compounds of this element are essential to this growth. The question of exactly what part the element plays in this plant development has not been really answered. Inorganic substances are thought to aid in producing those changes by which carbon dioxid and the other simple food substances are converted into the complex organic substances of the plant. However this may be in detail, it is known that potassium is found in the salts of organic acids, as is seen in such substances as the crystals found in certain plants which are potassium acid oxalates (KHC_2O_4). It is probably a part of other more complex organic compounds. When these compounds are burned, the potassium is left in the ash, principally as potassium carbonate. Many plants, or particular parts of plants, are quite rich in potassium compounds, such as the grape, leaves of sunflower, beet wastes, etc., and are the source of inorganic potassium compounds. These substances are oxidized, and the carbonate is separated from the ash by treating them with hot

water, which dissolves out the potassium carbonate and small amounts of the sulfate, chlorid, and silicate, with other soluble substances. This solution is evaporated to dryness, and the solid residue is the crude "potash" of the market. This crude material is purified by treating with a little water, which dissolves the readily soluble carbonate, and can therefore be separated by filtration from the insoluble portions. There remains some organic matter which is decomposed by heating the purified carbonate to red heat. The product is known as pearl ash from its color. The pure carbonate is not readily obtained from the pearl ash, and consequently some organic salt that can be obtained pure is used for this purpose. The tartrate is the one commonly used. The treatment is quite like that used in preparing pearl ash. The tartrate is burned, leaving the carbonate and a small amount of unoxidized carbon, which is removed by solution and filtration.

Since the discovery of the large deposits of potassium salt at Stassfurt, a large per cent of the potassium carbonate of commerce has been prepared from these compounds by processes similar to those used for preparing sodium carbonate. (See under SODIUM.) The salt crystallizes from water solutions in crystals containing three molecules of water. At 100° two-thirds of the water escapes. The other molecule is driven off at 130°.

Potassium carbonate is used in glass-making (which see), for preparing soft soaps, and as a source of many of the other potassium compounds. This carbonate and that of sodium are the only ones that cannot be decomposed at any readily produced temperature.

Potassium Acid Carbonate ($KHCO_3$). — This salt is prepared from the crude normal carbonate by passing carbon dioxid through a saturated solution of the latter salt. The reaction is —

$$K_2CO_3 + CO_2 + H_2O = 2\ KHCO_3.$$

The acid carbonate is not as soluble as the normal carbonate, and consequently separates out in the form of fine crystals. When these crystals are heated they are decomposed, and the normal carbonate (K_2CO_3), water, and carbon dioxid are driven off. The carbonate thus prepared is quite pure.

This compound has a number of names, such as the acid carbonate, bicarbonate, and saleratus. The term *saleratus* (sal, aërated) was applied to this compound because it was prepared by the action of a gas (an "air") on a salt. Under this name the compound was formerly used as a source of carbon dioxid in bread-making.

Potassium Sulfate (K_2SO_4).—The occurrence of potassium salts in the mineral deposits at Stassfurt has already been noticed. Potassium sulfate is found here associated with magnesium sulfate and chlorid, and is known as kainite, having the composition represented by the formula $MgSO_4.K_2SO_4.MgCl_2.6\ H_2O$. The compound is produced as a by-product in the manufacture of other chemicals. It is used in preparing potassium carbonate, common alum, and in fertilizers as the source of potassium.

Several other sulfates are formed, among which are the acid sulfate ($KHSO_4$) and the pyrosulfate. The acid sulfate corresponds to the acid carbonate. This salt is obtained by heating the normal sulfate (K_2SO_4) with sulfuric acid, or by heating such a substance as potassium (or sodium) nitrate with an excess of sulfuric acid. It is therefore a by-product in the manufacture of nitric acid. In the first case, 1 g. of sulfuric acid is used to 1.75 g. of the salt. When the acid sulfate is heated to 200°, two molecules give up a molecule of water, and become the pyrosulfate ($K_2S_2O_7$ or $K_2SO_4.SO_3$). This latter salt when heated to 600° is decomposed into potassium sulfate (K_2SO_4) and sulfur trioxid. Either one of these salts is a powerful chemical agent in acting on metallic oxids. It is much more active than sulfuric acid, since it is set free at a

temperature of 600°, while sulfuric acid vaporizes at 338°. It is used in decomposing insoluble minerals, like the clays.

Sulfurous acid forms similar salts; namely, the normal sulfite (K_2SO_3), the acid salt ($KHSO_3$), and the pyrosulfate ($K_2S_2O_5$ or $K_2SO_3.SO_2$).

The other salts of potassium have been referred to sufficiently already. They are the cyanids (ferro-, ferri-, and sulfo-cyanids), phosphates, and silicates. The three possible phosphates, KH_2PO_4, K_2HPO_4, and K_3PO_4, are all readily produced. These phosphates, with those of the other alkalis, are all soluble; and when the acid phosphates are heated, the hydrogen removes an atom of oxygen and leaves the meta- or pyro-phosphates according to whether the mono- or di-hydrogen salt is heated.

Potassium sulfid and potassium hydro-sulfid are closely related compounds of considerable chemical interest. When hydrogen sulfid is passed into a solution of potassium hydroxid, the following reaction occurs: —

$$KOH + H_2S = KSH + H_2O.$$

That is, the sulfur and oxygen exchange places. When a solution of the hydrosulfid is treated with an equivalent amount of potassium hydroxid, the normal sulfid is formed, although some authorities doubt whether this reaction occurs in water solution.

$$KSH + KOH = K_2S + H_2O.$$

The sulfid is also formed by reducing potassium sulfate with carbon. In water solution it absorbs oxygen from the air forming the thiosulfate ($K_2S_2O_3$),—

$$2\,K_2S + 2O_2 + H_2O = 2KOH + 2K_2S_2O_3.$$

When a solution of potassium sulfid is boiled with sulfur, the latter element is dissolved and a number of sulfids are formed. They are represented by the formulæ, K_2S_2, K_2S_3, K_2S_4, K_2S_5. These are all decomposed by acids setting sulfur free (milk of

sulfur) and forming the salts of the acid used and hydrogen sulfid. The water solutions of the normal sulfid dissolve other sulfids such as those of arsenic and antimony and tin. (See under AMMONIUM SULFID.)

SODIUM.

(See Part I., page 91, for first five topics, preparation excepted.)

The methods for the preparation of sodium that were in use until recently were practically identical with those used for potassium. The use of sodium in large quantities in preparing aluminium has called attention to the need of a cheaper and more expenditious method for its preparation. The result has been, the use of a new method, discovered by Castner, by which the metal can be produced much more readily. The essential differences of the new process are the preparation of a new carbon reagent, and the use of sodium hydroxid instead of the carbonate. The reagent is made by heating to a high temperature very fine iron filings with pitch. Air being excluded, the iron unites with the carbon, forming iron carbid (FeC_2). When cooled, this mass is broken up and thoroughly mixed with the hydroxid and then heated to about 850°. The reduction takes place at a lower temperature than by the older method (about 500° lower) and thus effects a considerable reduction in the cost of production. The great demand for sodium in the manufacturing industries, especially in preparing aluminium, in connection with the improved methods of manufacture have greatly reduced its cost. (One authority says that a kilogramme of sodium can be bought now for the price of a gramme thirty years ago.)

Compounds of Sodium.

Sodium and potassium are very closely related elements. In general, if any particular property is considered, the difference is found to be one of degree. Sodium is not so active, chemically speaking, as potassium. For example, sodium decomposes water readily, but the heat of the reaction is less, as is shown by the ready ignition of the hydrogen set free by potassium, while sodium under the same conditions does not usually ignite the gas. Both sodium and potassium have the property of setting hydrogen free from most compounds containing it, even from such a compound as ammonia, forming sodium amid (NH_2Na). Sodium is electro-positive towards all elements except potassium, cesium, and rubidium. (See later under CLASSIFICATION.) Consequently the facts here noted in reference to the sodium compounds will have to do principally with differences in the methods of preparation and in occurrence.

(*a*) **Oxids and Hydroxids.** — Sodium forms two oxids; namely, the normal oxid (Na_2O), and Na_2O_2 (sodium peroxid). This latter oxid has come into prominence recently as a laboratory reagent for oxidizing purposes. It is used principally to oxidize difficultly reduced ores and minerals such as those of lead, arsenic, certain iron ores, etc.

Sodium hydroxid is prepared in considerable quantities from the waste of sodium carbonate manufacture, but a large part of the commercial article is produced from sodium carbonate by the action of slaked lime, as was described under potassium. Sodium hydroxid is used in large quantities in soap-making (hard soap) as a reagent in the laboratory, as a cleansing agent, and in many of the other industries.

(*b*) **Salts of Sodium; Halogen Salts.** — The most abundant of the halogen salts is sodium chlorid, or common salt. It is widely distributed in the earth's crust and in natural

waters. Sea-water contains an average of about 3 per cent. The rain water coming in contact with the solid parts of the earth's crust dissolves out the sodium chlorid along with the other substances. These waters finally find their way to the oceans, which, therefore, become slowly (very slowly, it is true) more and more concentrated solutions of these salts. Salt also occurs in large masses as mineral deposits, which are known as rock salt. Such deposits are found in the United States in Kansas, Louisiana, Michigan, New York, and elsewhere, where it is often brought to the surface by natural springs or by being pumped from wells in concentrated solutions. It is also found in Europe in large quantities in many localities.

Salt is prepared from sea-water by evaporation or by concentrating the water to the point of crystallization of the salt; or the water from wells or springs is used, and similar processes of concentration and crystallization are employed; or it is mined from the solid salt deposits. In hot countries the first concentration of the solution is done by the sun's heat, and in cold countries the same result is reached by freezing the salt water and removing the ice, which is quite pure water. The evaporation is completed by artificial heat.

From what has been said of the origin of salt, of its natural deposition and accumulation, it would be expected that when it is prepared by the processes just described it would be impure. Such salt contains a variety of impurities, such as magnesium sulfate and chlorid, sodium sulfate, and small amounts of other sodium salts. A fact in reference to the salt that aids in its separation from its solution with other salts is that it is not very soluble in water, and also that it has about the same solubility in cold that it has in hot water. Thus, at 0°, 100 g. of water dissolve 36 g. of salt, and at 100° it dissolves only 3 g. more. Most of the substances in solution with salt in sea and other natural water are absolutely more soluble than it is, and

they are also more soluble in hot than they are in cold water. The " mother liquor " from salt manufacture is often the source of the iodids and bromids of both sodium and potassium. Some of the impurities found in the mother liquor, such as calcium sulfate and chlorid, magnesium sulfate and chlorid, sodium sulfate and potassium chlorid, separate out with the salt when it crystallizes. . Magnesium salts are always bitter in solution, and therefore they impart a bitter flavor to salt which contains a measurable amount of them. Magnesium and calcium chlorid, as we have seen, attract moisture, and if present in the salt, make it hygroscopic.

Ordinarily, salt crystallizes in cubes without water of crystallization, but below $-10°$ it crystallizes with two molecules of water, $NaCl.2\,H_2O$. The crystals inclose water, and, therefore, decrepitate when heated. A saturated solution of common salt contains 26.4 per cent at ordinary temperatures.

Salt is the source of all other compounds of sodium, and is used in the arts in many ways, *e.g.* in glazing the cheaper grades of earthenware. It is also the source of the chlorin in bleaching-powder and in hydrogen chlorid. It is estimated that the civilized portion of the human family make use of about 10 kg. of salt per year for each individual, and that about as much more is used in the arts.

Sodium Sulfate (Na_2SO_4); Crystals ($Na_2SO_4.10\,H_2O$). — Sodium sulfate is found in nature in many natural waters, and also in large deposits in Spain. It is produced as a by-product in many cases, and is one of the products in sodium carbonate manufacture (which see). It is commonly known as Glauber's salt. It is used as a purgative in medicine, and large quantities are used in glass manufacture.

Sodium sulfate presents some interesting peculiarities in reference to its solution and crystallization. A saturated solution of the salt contains, at 0° for every 100 g. of water, 5 g. of salt; at 10°, 9 g.; at 20°, 19.4 g.; at 30°, 40 g.; at 34°, 55 g.

of salt. This is true whether the salt is anhydrous, or whether it contains 10 molecules of water. Above 34° the solubility of the salt decreases, until at 100° only 43 g. are dissolved in 100 g. of water. Or a solution saturated at 34° will deposit crystals of sodium sulfate if the solution is boiled. These crystals are anhydrous. If a like solution is carefully cooled down to −8°, no crystallization occurs; but if there is added a crystal of the salt, immediate and very rapid crystallization occurs. Again, if a crystal, $Na_2SO_4.10\,H_2O$, is heated to 34°, it loses its water of crystallization. This loss of water occurs at ordinary temperatures, and the salt becomes a white powder, or it is said to have effervesced. This peculiarity (although the phenomena are not confined to this salt) of solutions finds its explanation in the fact just given; namely, that at temperatures above 34° the crystals, $Na_2SO_4.10\,H_2O$, do not exist, and the solubility that obtains above this temperature is that of the anhydrous salt, Na_2SO_4.

The other sulfates of sodium, $NaHSO_4$, $Na_2S_2O_7$, are, like the corresponding ones, of potassium. For sodium thiosulfate see Part I., page 229.

Sodium Nitrate ($NaNO_3$). — What has been said from time to time about the natural formation of potassium nitrate applies equally well to sodium nitrate. It is found in large quantities on the west coast of South America, and, from the fact that the government of Chili owns a large amount of these deposits, the substance is often called Chili saltpetre. It is a crystalline salt that is deliquescent in air, and although it contains, for the same mass, more oxygen than the potassium salt, it cannot take its place in gunpowder, because of this fact. It is, however, the source of nitric acid, and is used for fertilizers. Large quantities are shipped each year from Chili to the United States and Europe for these purposes.

Another important use of sodium nitrate is in the preparation of potassium nitrate. This formation depends on a principle

that has been spoken of several times before; namely, that when the saturated solutions of two soluble salts are brought together, if by exchange of bases, a less soluble salt is formed under the conditions such exchange takes place. The conditions are, in general, that one of the salts that is formed is about equally soluble in hot or in cold water, while the other is highly soluble in hot water, and only moderately so in cold water. The last condition is often made use of, on a manufacturing scale, in separating salts of the same kind; for example, potassium chlorid and sodium chlorid. The former is very soluble in hot water, but only slightly so at low temperatures. If, now, the solution of the mixed salts is evaporated, the sodium chlorid will be deposited after saturation is reached. The evaporation can be continued until the solution becomes saturated, or nearly so, for the potassium chlorid, when, on cooling, the potassium salt crystallizes out, leaving the sodium chlorid in solution.

In the preparation of potassium nitrate from sodium nitrate and potassium chlorid the same general facts obtain, as can be seen by examining the reaction in connection with the solubilities of the factors and products. (See under POTASSIUM NITRATE.)

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

Sodium Carbonate (Na_2CO_3); Crystals ($Na_2CO_3.10\,H_2O$). — Sodium carbonate occurs in nature in considerable quantities. It sometimes is held in solution in lakes, such as are found in Hungary, Egypt, and in Southern Russia. It is found in solid deposits in Asia and Africa, and also in the dry regions of the United States. The "alkali" plains owe their peculiar property to this salt. The name *natrium* is derived from *Natron*, the ancient name of one of these deposits. Its commercial source was originally the ashes of sea-weeds, and was, in general, prepared in the same manner as was potassium carbonate, from

wood ashes. (See K_2CO_3.) The carbonate for use in bread-making was, in fact, supplemented by the use of potassium carbonate. The supply of the latter salt being cut off by the exigencies of war, a prize was offered by the French authorities, in 1794, for the discovery of a process by which the sodium carbonate could be produced from common salt, or from substances that could be readily obtained in France. This led to the development of the process of Le Blanc. By this method the sodium for the carbonate comes from common salt, and the carbon dioxid from calcium carbonate.

Common salt is treated with sulfuric acid when the usual reaction occurs. The hydrogen chlorid is passed into water, and thus a valuable product, hydrochloric acid, is saved. The residue, called salt cake, which consists largely of sodium sulfate, is next mixed with carbon and calcium carbonate and heated to a high temperature. The reactions that occur may be studied in two parts, although in practice they occur simultaneously. At first the carbon acts upon this sulfate, completely deoxidizing it. The reaction is the one that generally occurs when carbon acts on a sulfate,—

$$Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2.$$

The sodium sulfid now reacts with the calcium carbonate, forming sodium carbonate and calcium sulfid,—

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The heat necessary for these reactions decomposes some of the calcium carbonate, so that the residue contains sodium carbonate, calcium sulfid, and calcium oxid. This mass is broken up and treated with water, which dissolves the sodium carbonate and small amounts of the soluble impurities that are formed during the reaction just described. After filtering out the insoluble residue and evaporating the filtrate to dryness, the impure carbonate that is left is ignited, and the product is

the crude soda of commerce. It is redissolved and crystallized, and then is known as "sal soda" and as crystallized soda. The pure crystallized carbonate contains 10 molecules of water. When the crystals are heated, they melt at 34°, and soon lose all but one molecule of the water of crystallization. At higher temperatures this molecule is driven off. The usual commercial form of the salt is the anhydrous form (Na_2CO_3). The compound does not decompose at any easily producible temperature, but fuses at red heat.

It will be noticed that this process requires the manufacture of sulfuric acid, and that all of this sulfur is finally combined in the nearly useless calcium sulfid. Consequently, considerable effort and study have been made to develop a process in which there shall be no waste material and that shall require no manufactured substances. In other words, to find a process that shall produce the compound at the lowest cost. Such a method has been found in the Solvay process. An outline of the method is of interest from this standpoint, at least.

The Solvay process for soda manufacture was somewhat crudely first brought out in 1861. It has been improved from time to time since, until it represents one of the most perfect methods in chemical technology. The sources of the sodium and of the carbonic acid radical are the same as in the Le Blanc process. Also magnesite, coke, and anthracite may be used. The process consists in forming ammonium acid carbonate (NH_4HCO_3) in a solution of sodium chlorid. It also depends on the relative solubility of the salts, according to the general facts described under sodium nitrate. The reactions are—

$$NH_3 + CO_2 + H_2O = NH_4HCO_3;$$

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

Sodium acid carbonate, or bicarbonate, is quite insoluble in water, 100 g. of which dissolves but 7 g. of the bicarbonate

at 0°. The increase in solubility of the salt as the temperature rises is but slight, since at 30° it is 10 g. of the bicarbonate for 100 g. of water. The ammonium salt is very soluble. The original supply of ammonia comes from crude ammonium chlorid, a waste product of gas works. The ammonium chlorid of the second reaction is heated with magnesium oxid (which may have been supplied by magnesite), which reacts like lime,—

$$2\,NH_4Cl + MgO = 2\,NH_3 + MgCl_2 + H_2O.$$

The by-product magnesium chlorid is decomposed by heat in presence of water, forming magnesium oxid (MgO) and hydrogen chlorid. In this manner the chlorin of the salt used at first becomes the useful product hydrochloric acid, and the magnesium oxid is ready to again free the ammonia.

Normal sodium carbonate is made from the acid salt thus produced by gently heating (about 100°), when carbon dioxid and water are driven off and the undecomposable normal salt is left. On the other hand, the bicarbonate can be prepared by passing carbon dioxid through a saturated solution of the normal carbonate. The normal salt at 20° is dissolved at the rate of 22 g. to 100 g. of water, while the same amount of water dissolves but about 10 g. of the bicarbonate.

Sodium carbonate stands close to sulfuric acid in commercial importance. It is used in soap-making, in glass-making, and as the source of nearly all other sodium compounds. Sodium carbonate is alkaline in reaction, and is readily decomposed by acids, even by very weak organic acids. A solution of this salt is employed in the laboratory to form the carbonates of other metals by precipitation.

Sodium bicarbonate is used as a source of carbon dioxid in baking-powders and in effervescing drinks. Its use in baking-powders is due to the fact that it will yield about one and one-third times as much carbon dioxid for the same mass of salt as the normal carbonate, and leaves as a residue half as much of

the sodium compound. (Write the reaction.) Its cheapness has almost entirely shut out the use of the corresponding salt of potassium as a source of carbon dioxid in bread-making. The carbon dioxid is set free in the baking-powder by acid compounds, such as tartaric acid, cream of tartar, alum ($K_2Al(SO_4)_2$), and the acid phosphate ($CaH_4(PO_4)_2$).

The reactions are —

$$2\ NaHCO_3 + H_2C_4H_4O_6 = Na_2C_4H_4O_6 + 2\ H_2O + 2\ CO_2;$$
$$NaHCO_3 + KHC_4H_4O_6 = NaKC_4H_4O_6 + H_2O + CO_2.$$

These two compounds can be mixed when thoroughly dry without setting up the reaction. The mixture is then mixed with the flour, and when the mass is wet the reactions take place, setting the gas free in the dough which holds it, and when the loaf is baked, the heat expands the gas and enlarges the loaf. One gramme of the carbonate will form about 260 cc. of gas measured at 0°.

Seidlitz powders are the bicarbonate and either tartaric acid or potassium acid tartrate. The proper proportions of each substance are prepared and each dissolved in water, and the two solutions are then mixed, which constitute the aperient liquid.

When solutions of each sodium and potassium carbonate are mixed and made sufficiently concentrated, there are formed crystals having the composition represented by the formula $KNaCO_3.12\ H_2O$. The dried salt is used as a fusion mixture, it being more effective than either carbonate alone.

Sodium Tetraborate ($Na_2B_4O_7$); Crystals ($Na_2B_4O_7.10\,H_2O$). — This salt is often called borax and is a salt of tetraboric or pyroboric acid ($H_2B_4O_7$). (See Part I., p. 340.) This compound is found in nature in certain bodies of water, located principally in Thibet and in California. Borax is prepared from the waters of the lakes, or it is made by neutralizing the native boric acid which is found in many volcanic regions. Borax is an antiseptic, and is used as a preservative. It is also used in

making soap and in the laboratory as a reagent for detecting metallic compounds. (See under the various metals, BEAD TESTS.) In general, when borax is heated with a base, the metaborate is formed. For example, —

$$Na_2B_4O_7 + 2\ NaOH = 4\ NaBO_2 + H_2O.$$

Other Salts of Sodium. — Like potassium, sodium forms salts with all of the acids, but most of the salts need no particular description. Phosphoric acid forms the three possible salts, according to the valence of the sodium and of the acid radical. Sodium silicate (Na_2SiO_3), or soda water-glass, is produced by fusing silicon dioxid (sand) and sodium carbonate. Other silicates are sometimes formed, depending on the conditions under which the fusing occurs. Sodium silicate forms a part of ordinary glass, and is used in artificial stone-making and in certain soaps.

AMMONIUM.

Several of the considerations that have led chemists to regard the group NH_4 as unit acting like a metal in the formation of compounds have been given in Part I., page 140. In spite of the doubt of the existence of an ammonium amalgam there mentioned, other facts that are favorable to the Berzilius ammonium theory may be given here. If the reaction between sodium-amalgam and ammonium chlorid be produced at a low temperature, there is formed a crystalline compound (in cubes) that is decomposed as the temperature rises. The products are ammonia and hydrogen, one volume of the hydrogen to two volumes of the ammonia, the result that would be expected if the group NH_4 were decomposed, —

$$2\ NH_4 = 2\ NH_3 + H_2.$$

Again, if these crystals of amalgam are placed in water, they are decomposed, mercury, hydrogen, and ammonia being set

free, the water becoming alkaline. This reaction therefore resembles the action of water on sodium amalgam; that is, in the latter case hydrogen, mercury, and an alkaline solution is formed, the alkalinity being due to the compound NaOH. Here it is due to NH_4OH.

$$HgNa_2 + 2\ HOH = H_2 + Hg + 2\ NaOH;$$
$$Hg(NH_4)_2 + 2\ HOH = H_2 + Hg + 2\ NH_4OH.$$

The compound NH_4OH has not been isolated, nor is it certain that the group NH_4 has, although it is claimed that such a compound has been produced by the action of ammonium chlorid on the compound of ammonia and potassium (NH_3K). Quite stable alkaline compounds have been produced by substituting known organic group like CH_3 (from marsh gas (CH_3H)) for the four atoms of hydrogen, forming such a compound as $N(CH_3)_4OH$. Whether this group or radical can be separated or not from its compounds, it is the amount of matter (hydrogen and nitrogen) that is exchanged for one atom of potassium or sodium or the amount that is equivalent to one atom of hydrogen in the formation of salts. The group is therefore univalent.

General Characteristics of Ammonium Salts. — (*a*) Salts of ammonium are all soluble in water, and generally crystallize without water of crystallization.

(*b*) Some of these salts are dissociated at quite low temperatures, but most of them are permanently decomposed by heat. When they are dissociated by heat, ammonia and the corresponding acid are formed. This is the case with ammonium chlorid, which becomes completely dissociated at 350°. This was one of the volatile compounds whose vapor density did not agree with what it was shown to be by a study of the compound by other methods. For example, from a study of its method of formation from ammonia and hydrogen chlorid, taken in connection with its percentage composition,

it is inferred that it contains at least one atom each of chlorin and nitrogen, and four atoms of hydrogen. The vapor density of the compound is 13.3, which corresponds to a molecular mass of 26.6+. But the proportion of the elements indicated by the analysis of the salt shows that the molecule must have a mass of 53.37, since there must be at least an atom each of nitrogen and chlorin, and, consequently, four atoms of hydrogen. This number is twice the molecular mass found by the vapor density method. If the vapor of this compound is brought under the appropriate conditions, it is found that it consists of free ammonia and hydrogen chlorid. It will be remembered that when this compound is formed, one volume of ammonia unites with one volume of hydrogen chlorid. Now the vapor density of a mixture of equal volumes of these two gases is 13.3 $\left(i.e.\ \text{of}\ \frac{18.18+8.5}{2}\right)$. Thus the abnormal vapor density of ammonium chlorid is readily explained by dissociation.

If the acid is non-volatile, and is not decomposed at the temperature of the disintegration of the salt, then ammonia is driven off and the acid remains. Ammonium sulfate decomposes into ammonia and sulfuric acid at a little above 140°, but at higher temperatures the acid is decomposed, and ammonia, nitrogen, water, and sulfur dioxid are formed.

Ammonium nitrate, which has been previously studied, is completely decomposed by heat (see Part I., page 233).

The bi- and tribasic acids, for example, often form salts, in which ammonium and some other base replace the hydrogen. When such salts are gently heated (provided the acid is non-volatile), ammonium is decomposed, and ammonia escapes, and an acid salt is left; but if highly heated, the pyro- or meta-salt of the non-volatile base is left. This is illustrated by magnesium ammonium phosphate ($MgNH_4PO_4$). The final product is often a very stable compound, —

$$2\,MgNH_4PO_4 = Mg_2P_2O_7 + H_2O + 2\,NH_3;$$
$$KHNH_4PO_4 = KPO_3 + NH_3 + H_2O.$$

Preparation of Ammonium Salts. — Most of the ammonium salts are prepared by neutralizing the corresponding acid with ammonia. The ammonia commonly used is an impure water solution, a waste product from illuminating-gas works. The resulting salt is quite impure, and is purified by crystallization or by sublimation, depending on the effect of heat on the salt, according to what has just been pointed out. Ammonium chlorid (NH_4Cl) is purified by this method. Ammonium sulfate is purified by crystallization.

Ammonium carbonate, another important salt of ammonium, is prepared by heating together calcium carbonate and ammonium sulfate or chlorid. The reaction results in the formation of calcium sulfate and a volatile product formed by the union of carbon dioxid and ammonia in the presence of a small amount of water. When the dry gases (two volumes of ammonia and one volume of carbon dioxid) are brought together, a solid compound is formed, known as ammonium carbamate. This compound is a salt of an acid that may be regarded as carbonic acid, in which one hydroxyl group is replaced by the group NH_2. It is represented thus: —

$$CO\begin{matrix}/NH_2\\ \backslash OH\end{matrix}.$$ The salt is, therefore, $$CO\begin{matrix}/NH_2\\ \backslash ONH_4\end{matrix}.$$

The product of the sublimation just referred to contains one molecule each of the carbamate and the acid carbonate (HNH_4CO_3). The latter salt is a crystalline salt that does not decompose in the air at ordinary temperature, but is easily decomposed at a slightly raised temperature.

The carbonate, on the other hand, decomposes if exposed to the air, giving off ammonia, and leaving the acid salt, HNH_4CO_3. The reaction is—

$$NH_2CO_2NH_4 + H_2O = HNH_4CO_3 + NH_3.$$

This decomposition is what occurs when the commercial salt is used as "smelling salts." When the commercial salt is dissolved in dilute ammonia water, the normal salt is produced.

These ammonium carbonates are used in the laboratory to form the insoluble carbonates, and in medicine for various purposes.

Ammonium sulfid is a valuable laboratory reagent, that is prepared by passing hydrogen sulfid into a solution of ammonia. (Note its use in the solution of the sulfids of arsenic, tin, and antimony.) The product depends on the amount of hydrogen sulfid used. A saturated solution contains the hydro-sulfid, $NH_4 - S - H$, while if to a given volume of the saturated solution a volume of ammonium hydroxid of the same concentration equal to the original volume of the saturated solution be added, the normal sulfid is produced. These sulfids dissolve sulfur, forming polysulfids. As a reagent these latter sulfids are known as the yellow sulfid.

Ammonium, sodium hydrogen phosphate (NH_4NaHPO_4), commonly called microcosmic salt, was formerly obtained from urine, hence its name, which signifies a little world, referring to man. It is now prepared from ammonium chlorid and disodium phosphate (Na_2HPO_4). Hot saturated solutions of the salts are mixed and allowed to cool, when there crystallizes out the salt, $NH_4NaHPO_4.4\,H_2O$. When this salt is heated, the compound is decomposed, ammonium and water are driven off, and sodium metaphosphate ($NaPO_3$) is left as a clear glassy residue. The metaphosphates unite with the oxids of metals, forming phosphates or pyrophosphates. The following reactions are typical: —

$$NaPO_3 + CaO = CaNaPO_4;$$
$$2\,NaPO_3 + K_2O = Na_2K_2P_2O_7;$$
$$2\,NaPO_3 + CuO = Na_2CuP_2O_7.$$

Advantage is taken of these reactions to recognize certain metallic oxids, especially when the fused mass is colored, as it is in the case of copper oxid. The tests are made in the same

manner as are the borax bead tests. The other salts of ammonium are of but little general interest.

Sodium and potassium form very few insoluble salts, and consequently are not generally separated from other bases by precipitation. Potassium and sodium may be recognized by what are called flame tests, and ammonium compounds by the odor and alkalinity of ammonia according to the next study.

Experimental Study, No. 39. — (*a*) Clean a platinum wire by thoroughly washing it in acids and water. Then wet it in pure hydrochloric acid, and heat red hot in the clear Bunsen flame. Repeat this latter direction until the flame is unchanged in color, when the wire is heated in it. Now to a solid sodium compound (or to a solution of such a compound) add a little hydrochloric acid, and dip the clean wire in the acid solution, and heat in the Bunsen flame. (The wire should be placed in the edge of the lower part of the flame; the color then mantles the whole flame.) This colored flame is characteristic of sodium in any of its compounds, although the halogen salts, like the chlorid, are most effective. Examine this flame, looking through thick blue glass.

(*b*) Proceed as in (*a*) with a pure compound of potassium. Be sure that the wire is thoroughly free from all sodium compounds. The color produced here is characteristic of potassium compounds. Examine this flame, looking through the thick blue glass.

(*c*) Mix the salts of the two bases, and examine as before. What is the effect of yellow light on that of the violet end of the spectrum when they are mixed? What is true of the red end of the spectrum? Mix the red light from strontium compounds with that of sodium compounds. How does the result compare with the "calcium flame"? Next study the flame, using the blue glass as in (*a*) and (*b*). What does the blue glass enable you to do by way of recognition of these elements?

(*d*) Treat some dry ammonium salt, like the chlorid, with a

solution of potassium (or sodium) hydroxid. Heat the solution to boiling, and test the escaping gases by sense of smell and with litmus. Compare with page 133, Part I. The result is characteristic of all salts of ammonium. The test is best made on the solid material, but a concentrated solution can be used.

CLASSIFICATION OF THE ELEMENTS.

Up to this time the study of the individual element and its compounds has had the chief consideration, since the learner must know the majority of the individuals of a system of classification of objects before the relations that determine the system can be fully comprehended.

The general methods of classification of objects must be used here as well as in the more strictly classificatory sciences like the biological sciences. Similarity must be used as the basis of inclusion, and dissimilarity as the ground for exclusion from any particular class. But the question naturally arises, similarity in what sense? We classify animals on the ground of similarity of organs and their functions, structural resemblances, etc. Chemical units or elements cannot be classified on such bases; but the possibility of resemblance must be in reference to properties, chemical and physical, and in the largest sense of this term *properties*. It should be noted that it is not identity of properties, but gradation of properties, that must be the basis of this examination and classification. For example, in Part I., page 126, the oxygen family is described, and some of the reasons given for bringing these elements together in a so-called family. These facts should be again carefully considered. The chlorin or halogen family is another case in point. Let the student bring these elements together and consider such properties as their specific gravities, atomic masses, state of aggregation, their chemical relations to each

other, and he will find excellent reasons for speaking of the halogens as a group of related elements.

These general resemblances have produced several families of elements that have been recognized for a long time.

A more comprehensive classification, however, is of comparatively recent origin. Some attempts were made in the early part of this century to discover some relations among the atomic masses of elements that might lead to their more general classification. Attention was called to many facts, such as the following: Taking a group of related elements like the chlorin family, arranged in the order chlorin, bromin, iodin, and add together the atomic masses of the first and third elements; divide the sum by 2, and the result is the atomic mass of the intermediate element. The same is true of lithium, sodium, and potassium, and several other groups. Again, there are groups, the members of which have very nearly the same atomic masses. When these groups were farther examined, it was found that there was a fairly constant difference between the atomic masses of the elements of any given group. In the group calcium, strontium, and barium there was a difference of about 48. These facts were brought out in the first of this century, before the atomic masses of many of the then known elements were accurately known, and quite a large number of elements had not then been discovered.

Without presenting the claims of all the more recent workers in this field of chemical study, it may be said that the studies of three men have developed our present knowledge of what is known as the periodic system of classification of the elements. In 1864 John A. B. Newlands, an Englishman, announced the law of Octaves, and in 1869 D. Mendeleeff and L. Meyer published, at about the same time, the periodic law according to which the elements are now classified.

It has been shown that a law, in the experimental sciences, grows out of a study of facts, and is a statement of a common

relation among these facts. The logical method of presenting this subject is, therefore, to bring together the facts, and from their examination to deduce the law, or show how the law was deduced. The end may be reached, however, by stating the law, and afterwards the examination of the facts upon which it depends can be made.

The periodic law, as stated by Mendeleeff, is as follows: "The properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence, or, expressing ourselves algebraically, form a periodic function of the atomic masses of the elements."

Lothar Meyer states this law thus: "If the elements are arranged in order of increasing atomic masses, the properties of these elements vary from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series."

A shorter statement of the law is this: "The properties of the elements are periodic functions of their atomic masses."

The statement of the law by Meyer needs no elucidation, since it employs simple terms, and thus explains the term *periodic function.* One quantity is said to be a function of another when one is so related to the other that a change in the former produces a change in the latter. In this case the atomic mass is the varying quantity that by its changes produces changes in the properties of the elements. It must be granted that the atomic masses of the elements depend upon the fundamental characteristic of the elements. The statement that "the properties of these elements vary from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series," expresses the idea of a periodic phenomenon. The varying quantity is the atomic mass of the elements, and the periodic fact is the varying of a given property up to a certain condition, or value, when a nearly identical value of the property returns again, and the changes are more or less closely repeated.

An examination of the elements will justify the statement of this law in the form that it is given. First, the elements standing at the extremes are hydrogen, the unit of mass, and uranium 240. The elements written in the order of the magnitude of their atomic mass, whole numbers being used, are: —

1	7	9	11	12	14	16	19	23	24	27	28
H,	Li,	Be,	B,	C,	N,	O,	F,	Na,	Mg,	Al,	Si,
31	32	35·5	39	40	44	48	51	52	55	56	
P,	S,	Cl,	K,	Ca,	Sc,	Ti,	V,	Cr,	Mn,	Fe,	
58.5	59	63	65	70	72	75	79	80	85	87	
Co,	Ni,	Cu,	Zn,	Ga,	Ge,	As,	Se,	Br,	Rb,	Sr,	
89	90	94	96	—	103	104	106	108	112		
Y,	Zr,	Nb,	Mo,	—	Ru,	Rh,	Pd,	Ag,	Cd,		
113	118	120	125	127	133	137	138	140			
In,	Sn,	Sb,	Te,	I,	Cs,	Ba,	La,	Ce;			

from this point to 173, Yb, there are places for several elements that are not yet discovered. The series continues, —

173	182	184	191	193	194.8	196.9
Yb,	—Ta,	W,	—Os,	Ir,	Pt,	An,
200	204	206.9	208	232	240	
Hg,	Tl,	Pb,	Bi, — — —	Th,	—Ur.	

Let us now examine this series in reference to certain properties.

(*a*) For the property of basicity and acidity. Beginning with lithium, an active base, it is readily seen from the knowledge already gained of these elements that this property grows distinctly less marked to carbon, which is never basic (except when combined with hydrogen). Boron is weakly acidic in character, which property becomes strongly characteristic of fluorin.

At this point in the series another basic element is encountered in sodium; there is an abrupt return to the original property, and a similar variation in the properties of basicity

and acidity occurs as the atomic mass increases. The culmination of the change is in the element chlorin, the strongly acid element. It is noticed that potassium begins another period which ends with bromin. Rubidium abruptly changes the phenomenon to basicity, the period ending again in iodin. It will be noticed that this wave-like change just described culminates with the seventh element, counting the first one in the two first periods and at the seventeenth element in the next two periods. A study of other chemical properties will show, in general, the same periods of change. Some of these facts will be noticed later on.

(*b*) The same periodic variability in physical properties may be noticed. A physical property that is commonly considered here is that of the specific gravity of the elements. The result of the examination for this property of the first two long and short periods established by the study just made can be tabulated thus: —

	+	+	−	−	−	−	−	+	+	+
	Li	Be	B	C	N	O	F	Na	Mg	Al
Sp. Gr.	.59	1.85	2.68	3.3	3.(?)	2.(?)	1.5(?)	.97	1.74	2.56
A. V.	11.9	4.9	4.	3.6	5.(?)	8.(?)	13.(?)	23.7	13.9	10.6

	−	−	−	−	+	+	+	−	−	±
	Si	P	S	Cl	K	Ca	Sc	Ti	V	Cr
Sp. Gr.	2.49	2.3	2.04	1.38	.86	1.57	2.6(?)	3.7(?)	5.5	6.8
A. V.	11.4	13.5	15.7	15.6	45.4	25.4	17.	13.	9.3	7.7

	+	+	+	+	+	+	+	±	−	−
	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Sp. Gr.	8.	7.8	8.5	8.8	8.8	7.15	5.96	5.47	5.67	4.60
A. V.	6.9	7.2	6.9	6.7	7.1	9.1	11.7	13.2	13.2	17.

	−	+	+	+		±	−	−	+	+
	Br	Rb	Sr	Y		Zr	Nb	Mo	Ru	Rh
Sp. Gr.	2.97	1.52	2.50	3.60(?)		4.15	7.06	8.60	12.26	12.10
A. V.	26.9	56.1	34.9	25.(?)		21.7	13.	11.1	8.3	8.5

	+	+	+	+	±	−	−	−	+	+
	Pd	Ag	Cd	In	Sn	Sb	Te	I	Cs	Ba
Sp. Gr.	11.5	10.5	8.65	7.42	7.29	6.70	6.25	4.94	1.88	3.75
A. V.	9.2	10.2	12.9	15.3	16.3	17.9	20.2	25.6	70.6	36.5

	+	+
	La	Ce
Sp. Gr.	6.2	6.7
A. V.	22.5	21.0, etc.

The second series of numbers represents what is called the atomic volumes of the elements. This is the quotient of the atomic mass divided by the specific gravity. This number also expresses the volume, in cubic centimeters, of the element in the solid state that is occupied by the mass, in grammes, represented by the number expressing the atomic mass of the elements. In other words, 23 g. of sodium will occupy 23.7 cc. of space.

Before proceeding further it may be well to give the tables of the classification of the elements, according to Mendeleeff, which most clearly brings out the relations expressed by the periodic law. The tables are but slightly changed from those given in Mendeleeff's "Principles of Chemistry."

General Facts Emphasized by Tables I. and II. — It will be noticed that in Table II. the elements are arranged in the order of their atomic masses, beginning at lithium and passing vertically downward to chlorin, and then returning to the element potassium, an element closely resembling lithium. When bromin is reached, another return is made to rubidium, when the changes occurring in the preceding period are, in general, repeated.

Again, note that the element beginning each period is strongly basic, while the one at the end of the period is acidic in character. The first period is consequently divided into two short periods, as is shown by the table. In the smaller periods, the change from the basic element to acidic is quite regular. The

TABLE No. 1.

		GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.		
Hydrogen compounds.		—	—	—	MH_4	MH_3	MH_2	MH			(M_2H)
Highest salt-forming oxids.		M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_3	MO_2	MO
Periods.	Series.	H 1									
1st	1st	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19			
2d	2d	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.4			
3d	3d	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	CO 58.5	Ni 59
	4th	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80			
4th	5th	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	—100 (?)	Ru 103	Rh 104	Pd 106
	6th	Ag 108	Cd 112	In 113	Sn 117	Sb 120	Te 126	I 127			
5th	7th	Cs 133	Ba 137	La 139	Ce 140	Di 142	—	—	—	—	—
	8th	—	—	—	—	—	—	—			
	9th	—	—	Yb 173	—	Ta 182	W 184	—	Os 191	Ir 193	Pt 196
	10th	Au 167	Hg 200	Tl 204	Pb 206	Bi 210	—	—			
	11th	—	—	—	Th 232	—	U 240	—			

TABLE No. II.

GROUPS.	TYPICAL OR 1st SMALL PERIOD.	1st.	LARGE PERIODS.			
			2d.	3d.	4th.	5th.
I.	Li 7	K 39	Rb 85	Cs 133	—	—
II.	Be 9	Ca 40	Sr 87	Ba 137	—	—
III.	B 11	Sc 44	Y 89	La 139	Yb 173	—
IV.	C 12	Ti 48	Zr 90	Ce 140	—	Th 232
V.	N 14	V 51	Nb 94	Di 142	Ta 182	—
VI.	O 16	Cr 52	Mo 96	—	W 184	Ur 240
VII.	F 19	Mn 55	—	—	—	—
		Fe 56	Ru 103	—	Os 191	—
VIII.		Co 58.5	Rh 104	—	Ir 193	—
		Ni 59	Pd 106	—	Pt 196	—
I.	H 1 Na 23	Cu 63	Ag 108	—	Au 198	—
II.	Mg 24	Zn 65	Cd 112	—	Hg 200	—
III.	Al 27	Ga 70	In 113	—	Tl 204	—
IV.	Si 28	Ge 72	Sn 118	—	Pb 206	—
V.	P 31	As 75	Sb 120	—	Bi 208	—
VI.	S 32	Se 79	Te 125	—	—	—
VII.	Cl 35.4	Br 80	I 127	—	—	—
	2d Small Period.	1st.	2d.	3d.	4th.	5th.
			Large Periods.			

first two long periods, however, do not exhibit this regularity of change with the same distinctness, since iron, cobalt, and nickel very closely resemble each other. These facts are brought out by a study of Table I. The remaining periods are not complete, and between cerium and ytterbium, 140 and 173, there are undoubtedly several undiscovered elements. There is probably another element between molybdenum and ruthenium, but with this exception, the two short periods, and the first two long ones are complete. Periods 3, 4, and 5 are quite incomplete, but some of the places have already been

filled by the discovery of rare elements, and others will undoubtedly be found to fill all these vacancies.

Table I. shows the elements arranged in the order of their atomic masses as before; *i.e.* beginning with lithium and passing to fluorin in the horizontal direction to the right, the elements are arranged in the order given on page 304. The next element in the vertical column is sodium, but that is like lithium, and this is placed under lithium, and the second short period is written under the elements of the first period. By this arrangement, the elements that most closely resemble each other are found in the vertical columns. The elements found in any horizontal row are designated a series, and the vertical columns constitute groups. The large periods of Table II. are thus broken up into shorter ones. Thus the period beginning with potassium is in two series. Copper, which begins the fifth series (second of this period), does not very closely resemble potassium (although it has some properties that ally it with Group I.), and it, with silver and gold, constitutes a subgroup.

The fourth and fifth series have between them the elements cobalt, nickel, and iron, which are very much alike, and are placed in a group by themselves. The fifth and sixth and ninth and tenth series have similar small groups.

There are several irregularities in the arrangement of the elements just given, but it is not the province of an elementary work to discuss them, or to attempt their explanation.

The reader should study these tables for the purpose of discovering some of the relations among the elements that are brought out by these arrangements of the elements.

(*a*) Show that the value of any given property is, in general, the average of the values of the property of the two elements which are next to it on either side, in the series or in the group, — say melting-point, atomic mass, specific heat, etc., — taking, for example, such elements as zinc, strontium, and cadmium for the atomic mass.

(*b*) A study of the periods; for example, the first long period. What changes occur in the metallic character of the elements up to manganese? How do the next three elements compare with manganese and chromium in reference to their metallic character? Note the facts in reference to this character with the remainder of the periods.

(*c*) Taking into account the positions in the periodic system of calcium, strontium, and barium, what should be their relative chemical characteristics, remembering that rubidium and cæsium are more basic than is potassium?

(*d*) Note the valence of the different groups and series (*i.e.* those already studied), especially the lowest and highest valence. (Use hydrogen compounds, or those of chlorin, when no compound with the former element is known.) What prediction can be made in reference to the rare elements not studied? If Series II. be taken as determining the valence for the groups, what valences will they have?

(*e*) Compare, in reference to chemical properties, the odd and even numbered series with each other; also the members of the odd series with each other. Same for the even series.

(*f*) Make a table of the oxids of the elements studied according to groups, taking the highest valence of each group as a basis. Double the second and fourth groups; what might you infer in reference to the oxids of the rare elements?

(*g*) Study the electro-chemical properties.[1] (See table on page 304.)

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[1] In the earlier part of this century, Berzelius and others taught that the elements were arranged in a simple series, in which oxygen stands first, as the most strongly negative element, and potassium (now cesium) is placed at the other end of the series, as the most strongly positive element. Many of the facts in reference to the action of an electric current on the elements in binary compounds have been already noticed. For example, in the electrolysis of the chlorids of the alkaline earths, the base is attracted to the negative pole, and the chlorin is found at the positive pole. It was thought that all elements were in one or the other of two classes; *i.e.* an element was either positive or

Note that the elements are in two classes; namely, those that are electro-positive and those that are electro-negative.

Compare the change of electro-chemical character with the basic character. What is true of the electro-chemical character of the element, and the atomic masses of the elements? (Whether basic or acidic.) What is true in reference to the stability of the oxids and chlorids of the more strongly positive elements? Same question for the less positive elements. What is true of the negative elements in reference to this question?

Magnetic properties have been found by Carnelley to exhibit a periodic character similar to the electro-chemical properties of the elements.

Application of the Periodic Law. — If this generalization is accepted, it enables the chemist to determine the properties of rare and even of unknown elements. For example, when Mendeleeff announced the law, he predicted that new elements would be found to fill the then existing gaps between aluminium and indium, silicon and tin, and boron and yttrium. He gave the properties of three elements in detail. The three elements have since been discovered, and have been found to agree very closely with his prediction. Gallium, scandium, and germanium are the elements. They were known as eka-aluminium, eka-

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negative. Therefore, compounds were composed of two parts, — namely, a negative and a positive part, — and when a compound was formed, the result was somewhat like the action of the negative and positive poles of a magnet.

It is now known that there is a marked difference in many cases between the electrical relations among the elements and chemism or chemical affinity. An element may be electro-chemically positive towards one element and negative towards others. The relation is, therefore, purely relative, yet it is in many cases one of degree. For example, zinc (positive) will replace copper (positive), and chlorin (negative) will set free iodin or bromin from nearly all of their binary combinations. In general terms, however, the oxids and hydroxids of the positive elements are basic, while the corresponding compounds of the negative elements are acidic, or they form acids. This relation is now measured by the heat of formation; *i.e.* chlorin sets bromin free from its combinations because the heat of formation of the chlorin is greater than it is for the bromid, etc.

boron, and eka-silicon, in the order named. Other vacant places will, no doubt, be filled by the discovery of other rare elements, as more refined methods of recognition and separation are perfected. There is probably an element resembling molybdenum and ruthenium, having an atomic mass between 96 and 103. Also note the wide gap between didymium, 142, and ytterbium, 173.

The periodic law has been useful in fixing the properties of certain elements, and especially that of their atomic mass and valence. The equivalent of uranium was found to be 120, and, therefore, its atomic mass is this number, or it is some multiple of it. This would place the elements between tin and antimony. Its properties would not permit it to be placed here. Twice this equivalent was therefore taken. This atomic mass agrees with the result obtained from its specific heat. The same facts have been shown for various other elements, such as cesium and tellurium. It is a general truth, that, given the atomic mass of an element, and the properties of the element and its compounds become known. In general, also, the converse of this truth is true, and the periodic law thus becomes a great aid in fixing the atomic masses of the elements.

PERIODIC GROUPS.

(*a*) **Group I.** — This group is often divided into two sub-groups, as is indicated in the tabular statement. Sub-group A is composed of the elements lithium, sodium, potassium, rubidium, and cesium. Sub-group B includes the elements copper, silver, and gold.

Sub-group A. — Of this "sub-group," the elements sodium and potassium have already been studied. The other members of this sub-group are rare elements, although lithium is widely distributed in minute quantities in rocks and in natural waters.

Here only the salient properties of all the elements of the sub-group will be brought together. In order to be concise, these properties will be tabulated.

	Atomic Mass.	Melting-Point.	Specific Gravity.	Atomic Volume.
Lithium	7.01	180°.	.594	11.9
Sodium	23.	95.5	.972	23.7
Potassium	39.03	62.5	.865	45.5
Rubidium	85.2	38.	1.52	56.2
Cesium	132.7	26.5(?)	1.88(?)	70.7

Note that the increase of the atomic volume is accompanied by a decrease in the melting-point of the members of the sub-group; that the atomic mass is one-half the sum of the atomic masses of the element just preceding and following it.

		Colors.	
Lithium quite ductile.	Not volatile at red heat.	Flame red.	Softness follows melting-point.
Sodium very ductile at 0°.	Volatile at red heat.	Yellow.	
Potassium brittle at 0°.	A gas at dull red heat.	Violet.	
Rubidium.	Lower temp.	Red.	
Cesium.	Still lower temp.	Blue.	

These elements are all univalent and form the same class of compounds, having the same general formulæ. The general chemical character of these elements is shown by the heat of formation of similar compounds. For example, those of the chlorids are

$$(Li_2, Cl_2) = 187{,}620 \text{ cal.}; \quad (Na_2, Cl_2) = 195{,}380 \text{ cal.};$$
$$(K_2, Cl_2) = 211{,}220 \text{ cal.},$$

and the others, with an increasing heat of formation, although they have not been carefully determined. What is true here

is true of the other compounds. Lithium decomposes cold water slowly; sodium, somewhat rapidly; potassium, quite rapidly; rubidium, very rapidly; and cesium, explosively.

Lithium is quite like magnesium and the alkaline earth metals. It is also more like sodium than it is like the other three elements of the sub-group.

These metals are all found together in nature, although the latter two are in very minute quantities.

Sub-group B.[1]—The elements of this sub-group, copper, silver, and gold, are sometimes included in the eighth group. The elements of the sub-group A are the most basic of all the elements, and are therefore very active, chemically speaking. The elements of sub-group B, however, are not strongly basic, nor are they chemically active elements. Gold, in fact, is acid towards the stronger bases, such as potassium. The aurates, like $KAuO_2$, are examples of these compounds. This sub-group bears the same relation to the alkali group that several of the other secondary groups bear to their main group. For example, taking the atomic masses for comparison, the relation is shown by the following table:—

Na 23.	Mg 23.9	Al 27.	Si 28.
Cu 63.2	Zn 64.9	Ga 69.8	Ge 72.3
Ag 107.6	Cd 111.9	In 113.4	Sn 117.
Au 196.2	Hg 199.8	Tl 203.6	Pb 206.

Again, this sub-group is a transitional or an intermediate one, as is seen by noticing some of the physical properties of this group and those of the eighth group. Such properties as their atomic volumes, conductibility of electricity, fusibility, and volatility are good illustrations. Platinum, palladium, and nickel are not volatile, and fuse at a very high temperature, while gold, silver, and copper are much more fusible, and are, there-

[1] Tables of properties like those given for sub-group A should be prepared by the learner.

fore, connectors to mercury, calcium, and zinc, which fuse readily and are volatilized.

The elements of sub-group B are univalent, and are thus connected with sub-group A. Silver hydroxid is also sufficiently soluble to change litmus paper. Silver is always univalent. Gold is also trivalent.

The apparently anomalous position of the sub-group B is in part explained by some general considerations, some of which have just been referred to. These three elements introduce the odd-numbered series, each of which is connected to the even series by a group of elements consisting of three analogous elements, the members of which are closely related to each other, and this relation or analogy is similar in each case; that is, the analogy between nickel and iron is much the same as that between palladium and ruthenium, and between platinum and osimum. Again, the transition from an odd series to an even series is always abrupt, as an examination of the series will show. For example, chlorin to potassium and manganese to copper.

The general stability of compounds of this sub-group is shown by the heat of formation of the chlorids.

$$(Cu_2, Cl_2) = 65{,}600 \text{ cal.}$$
$$(Ag_2, Cl_2) = 58{,}600 \text{ cal.}$$
$$(Au_2, Cl_2) = 11{,}600 \text{ cal.}$$

Two members of group I. are absent; namely, elements to introduce series 9 (atomic mass about 156) and series 10 (atomic mass about 170).

Group II. — The elements of this group have all been studied except beryllium, and their properties can consequently be brought together as has been suggested in group I. This group, like all of the groups except group VIII., is divided into two sub-groups, A and B, the former sub-group consisting of elements of the even series, and the latter of the odd series.

There are the same gaps in these sub-groups as there were in those of group I.

Beryllium, the first member of sub-group A, has an atomic mass of 9.08; is a white metal, having a fusion point higher than that of calcium; specific gravity, 1.7; not oxidized in air; and is only oxidized superficially when heated. It requires red heat before it decomposes water. Compare with the other members of the sub-group in reference to these properties. Its oxid does not form the hydroxid on the addition of water. (Compare the other members of the sub-group.) Its hydroxid is quite insoluble in water.

The relative basic character of the elements and stability of their compounds are shown by the following facts: —

Beryllium hydroxid,		$Be(OH)_2$,	decomposes	at	about	300°.
Magnesium	"	$Mg(OH)_2$,	"	"	"	450°.
Calcium	"	$Ca(OH)_2$,	"	"	"	530°.
Strontium	"	$Sr(OH)_2$,	"	"	"	650°.
Barium	"	$Ba(OH)_2$,	fuses without decomposition.			

Like sub-group A of group I., this sub-group is naturally divided into two sections, — namely, beryllium and magnesium, — which resemble each other more closely than they do calcium, strontium, and barium. The latter three elements, the alkaline earths, have many analogies, and their corresponding compounds present marked gradations of properties. (Note such properties as the solubilities of compounds, atomic masses, valence, etc.)

Sub-group B. — Magnesium might well be included in this sub-group, since it resembles zinc and cadmium nearly as closely as it does the members of sub-group A. Mercury has many properties that are like those of gold. These elements hold similar positions in the last portions of long periods. Barium, calcium, and strontium occupy the same positions in the first part of the long periods. (Compare these elements

in reference to atomic mass, melting and boiling point, specific gravity, atomic volume, and other physical and chemical properties.)

Zinc oxid, like magnesium oxid, is slightly soluble in water, forming zinc hydroxid ($Zn(OH)_2$), and, like the magnesium hydroxid, it is alkaline to litmus. Magnesium oxidizes readily, zinc less so, and mercury least so of all the group.

The members of group I. are practically always univalent, excepting gold; those of group II. are always divalent, except mercury. Group II. is less basic than group I.

Group III. — The elements that constitute this group are rare elements with the exception of boron and aluminium. Only a few of the properties of many of these rare elements have been determined. The members of the odd series, however, have been studied to a considerable extent.

It will be noticed that boron stands between beryllium and carbon in atomic mass, and by its position it would be expected to possess slight, if any, basic properties. Its oxid (B_2O_3) approaches closely to a neutral oxid. It has feeble acid properties and a still feebler basic character. The preceding groups have been introduced by a comparatively inactive base, and have been followed by a more active one. This group follows this law. Aluminium is not as strongly basic as magnesium, but it is sufficiently basic to form salts with all but the weakest acid. It, however, forms compounds with strong bases. The odd series becomes more basic as the atomic mass increases. The properties of the members of the sub-group that are useful for comparison may be summarized as follows: —

Atomic masses as they are given in the table. Physical properties: aluminium, ductile, malleable, hard, not brittle, melts at 700°, specific gravity 2.6, atomic volume 10.5. Gallium, slightly ductile, slightly malleable, hard, rather brittle, melts at 30°, specific gravity 5.9, atomic volume 11.8. Indium, not ductile, soft, melts at 176°, specific gravity 7.5, atomic

volume 15.2. Thallium, ductile, soft, quite malleable, melts at 290°, specific gravity 11.8, atomic volume 17.3.

Chemical properties: aluminium, not readily oxidized even at high temperatures. Gallium oxidizes at red heat, but only on the surface of a mass. Indium oxidizes at about 200°. Thallium oxidizes in air at ordinary temperatures.

It is thus seen that the group presents the same general changes of character as have the preceding groups.

Group IV. — The principal elements of this group are carbon, silicon, germanium, tin, and lead. The properties of all these elements except germanium have been already studied. Germanium is in the odd series or in sub-group B, between silicon and tin, and consequently should have a specific gravity of about 5 (5.46), a melting-point of about 800°–900°; it should be more metallic than silicon, and less so than tin; in other words, it is rather indifferent both as a base and as an acid-forming element; if it forms a compound with hydrogen, it should be very unstable (none is formed); it should unite with the halogens to form stable compounds that are volatile without decomposition. $SiCl_4$ and $SnCl_4$ vaporize at 59.6° and 120° respectively, and therefore the corresponding chlorid of germanium ($GeCl_4$) should boil at a temperature not far from 90°–(86°). From the facts as to its basic character, hydrochloric and sulfuric acid should have but little action upon it, and nitric acid should only oxidize it. In its valence it should be quadrivalent and might possibly be divalent.[1]

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[1] The student should examine this group and the remaining four groups, studying and tabulating such facts as the following, especially with reference to the elements that have been considered, and the determination of the properties of the rare elements:

(*a*) Such properties as atomic volume, etc., that have been noticed for the groups already studied.

(*b*) Valence of the elements — especially the highest and lowest valence of the elements of the groups. Note the variability as the atomic mass increases.

(*c*) The formation of oxids and their arrangement in groups. Their character as to stability, basic, or acidic character.

It will be profitable for the student to predict the properties of such elements as molybdenum, wolfram, and uranium, taking their places in the system of classification as fixed, and then test the results by referring to some larger works, like Remsen's *Chemistry*, Advanced Course, or Roscoe and Schorlemmer's *Treatise*, Volumes I. and II., Part II., for a confirmation of the properties given these elements. The reader should note that the older classification corresponds in many cases with that of the periodic system. The halogens, the oxygen family, the alkaline earths, etc., are good examples. Many properties of the elements are being investigated at present, in the light of the periodic law. Such facts as the melting-points of the elements, and those of their salts, heat of formation of the salts, etc., are among those that are receiving especial attention.

QUALITATIVE ANALYSIS.

Chemical Analysis. — Chemical Analysis, as the term is applied in inorganic chemistry, is studied under two divisions; namely, qualitative and quantitative analysis. Qualitative always precedes quantitative chemical analysis, since the latter term answers the question, how much? and the knowledge of what the matter is must be determined before this question can be answered.

Objects and General Methods of Qualitative Analysis. — The purpose of qualitative analysis is to determine what a given

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(*d*) Study the halogen compounds, especially the chlorids of the fifth and seventh groups, in reference to stability, action of water on, etc.

(*e*) Examine the fifth, sixth, and seventh groups in reference to their hydrogen compounds; their stability, acid or basic character, etc. Note the effect of the addition of hydrogen on the basic properties on these elements.

(*f*) Study the relation of manganese and chromium to their respective groups. Note it especially in connection with their higher oxids. Note the effect on the basic character of these elements as the valence increases. Compare with iron and other elements on this latter point.

substance is, in terms of known matter. It therefore implies that certain forms of matter are known, and that unknown matter can be so changed that it takes on these known forms, or that it possesses certain recognized properties. The student has already learned that the different kinds of matter are recognized by physical and chemical properties. Further, that the properties of matter must be first learned before identity can be established between two pieces of matter. For example, a knowledge of what iron is must be gained before any unknown matter can be declared to be iron. (See pages 18 and 31, Part I.) It is evident that a careful and conscientious study of matter for the purposes indicated must precede qualitative analysis.

Matter has been studied in the form of elements and compounds, and these compounds are principally either the oxids, hydroxids, acids, or the salts of these acids. Consequently, these different substances must be recognized by certain physical properties, or by certain chemical changes that are characteristic. For example, a substance that suggests the element silver might be determined to be, or not to be, silver, by its physical properties, such as color, hardness, specific gravity, ductility, etc. Again, a pure white powder could not be recognized as sodium carbonate by its physical properties. We must appeal to its chemical properties. Such a substance is treated with an acid, and it is found that a gas escapes. The gas is recognized as carbon dioxid by its own characteristic properties. There is, again, the appeal to our knowledge, and it is known that the white powder is a carbonate, and therefore the salt of some metal. Its solubility is next examined, and it is found to be soluble in pure water, and, in general, it must be one of the alkaline carbonates, since only these carbonates are readily soluble in water. Some of the solution is used for the flame test, and the yellow color of the Bunsen flame shows that the metal sodium alone is present, and, consequently, that the com-

pound is sodium carbonate, Na_2CO_3. In the cases considered, there has been but one substance present, and the task has been to recognize it by one or more properties.

One more general case must be considered, — namely, the one of mixture, — more or less intimate, in which several substances may be present. There are some substances that give, with the appropriate reagents, results that are sufficiently characteristic for recognition. For example, iron is generally determined without reference to what other substances are present. (See Experimental Study, No. 21.) But most compounds (or elements) must be separated, as a whole, from others, or there must be the removal of some part of a given compound.

Salts are determined in two parts, — namely, the metal and the acid, — and usually by the combination of each part in a known compound before its identification can be made complete. For example, a mixture containing lead nitrate and silver nitrate is treated with a solution of sodium chlorid, and a white precipitate of lead and silver chlorids is formed. It is known that lead chlorid is soluble in hot water, while the silver chlorid is not. The lead of the soluble chlorid forms characteristically colored precipitates, with potassium iodid and chromate, and is thus recognized. Silver chlorid has just as characteristic properties, and is thus recognized.

The problem of qualitative analysis is therefore one of separation of an element, a compound, or of some part of a compound, and a recognition or identification of the same by means of the characteristic properties which each substance possesses.

Special Methods of Analysis. — The various laboratory studies that have been made of the elements and their compounds have developed, to a certain extent, two methods of qualitative analysis; namely, the dry and the wet methods.

(*A*) *The Dry Method.* — By the dry method, high heat alone, or heat and some dry reagent are used. This method will not

be very fully developed, but some of the methods that have been already used will be brought together here.

The Action of Heat Alone. — The action of heat on a substance has been referred to under volatilization, dissociation, decomposition, etc. It can be applied in qualitative analysis in several different ways. For example, mercuric oxid when heated is decomposed into mercury and oxygen. The latter, being a gas at lower temperatures than mercury, escapes, and the metal is left on the cooler parts of the vessel in which the decomposition occurs.

I. *The Use of Heat Alone.* — Many substances are volatilized without decomposition at high temperatures, and thus can be separated from non-volatile substances. This process, called sublimation, may therefore be used for separation, or as an aid in separation of such volatile substances. Examples: NH_4Cl and $HgCl_2$.

Many substances change color when heated to temperatures less than red heat, and these are often characteristic facts to be used in recognition of such substances.

(*a*) Suppose a mixture of ferric oxid and ammonium salts is made, and it is heated in a tube (hard glass best), what is the effect on the mixture?

(*b*) What is the effect of heat on the following substances heated in a tube, as in (*a*) : chlorates, bromates, iodid, sulfites, nitrates, halogen salts of mercury, salts of cobalt and nickel, oxids of zinc, lead, bismuth?

(*c*) Suppose water condenses on the cool parts of the tube in which a substance is heated (no organic matter being present), what may be its sources, provided the mixture is neutral? Suppose hydroxids are present, what is left in reference to these compounds?

II. *The Action of Heat and Some Reagent.* — The reagents that are commonly used are carbon (charcoal), carbon and sodium, or potassium carbonates. Sodium or potassium car-

bonate may be used alone. The carbon may be mixed with the given substance, and the mixture heated in a tube as before, or what is most commonly done, the substance is heated on charcoal alone, or with sodium or potassium carbonate. In this case the flame used to heat the substance is also a reagent. (See under FLAME and the various studies. Bring together the characteristic results of such examination.) What is the use of each reagent? Suppose an insoluble sulfate is heated with sodium carbonate, what will occur?

III. *Flame Test.* — Review and bring together these tests.

IV. *Bead Tests.* — Same as under flame test. (For further results see larger works, like Prescott and Johnson's Qualitative Analysis.)

(*B*) *The Wet Method.* — The first conditions to be met in using this method, as its name implies, is the solution of the substance to be analyzed. The terms *solution*[1] and *solubility* are used in the sense heretofore employed.

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[1] When a substance is said to be soluble, reference is made to its solution in water. When its solubility in acids is referred to, the acid will be mentioned. For example, magnesium carbonate is soluble in hydrochloric acid. The term *solution* is a somewhat variable one when applied to solubility in water (see page 250). There are no definite limits which determine when a substance is soluble and when it is insoluble. Adjectives like *very* and *partially* are often used to indicate degree of solubility. For example, 1 g. of magnesium sulfate is soluble in 3 g. of water; calcium sulfate requires 400 g. of water for the same amount of salt; strontium sulfate requires 8,000 g., and 1 g. of barium sulfate is dissolved in 420,000 g. of water. Or stated in another way, 20 cc. of water will dissolve 6.66 g. of $MgSO_4$, .05 g. of $CaSO_4$, .0025 g. of $SrSO_4$, and .00005 g. of $BaSO_4$. Calcium chlorid dissolves in the water that it absorbs from the atmosphere, one part of salt not requiring more than one part of water for complete solution. The latter salt is spoken of as very soluble, while calcium sulfate is said to be partially soluble. Barium sulfate is called insoluble. Compounds that are much less soluble than calcium sulfate are considered insoluble. Referring to these facts of solubility, it is seen that the precipitation of a given substance is never absolutely perfect, although it is very nearly so in many cases. The precipitation of lead as lead chlorid, the removal of this salt by filtration, and the formation of lead sulfid in the filtrate by hydrogen sulfid is a further example.

The wet method of qualitative analysis is, in general, based on solubility. Consequently, a knowledge of the solubility of the principal compounds is essential to an intelligent use of this method. The learner should therefore be able to answer such questions as the following, the facts being derived from the previous study: —

(*a*) What is the solubility of the metals?

(*b*) What is the solubility of the oxids and hydroxids of the metals studied?

(*c*) What is the solubility of the salts of the metals? *e.g.* chlorids, iodids, sulfids, sulfates, phosphates, carbonates, etc.

(*d*) What is the solubility of the sulfids, phosphates, carbonates, hydroxids, and oxids in hydrochloric acid?

(*e*) What is the solubility of the compounds of (*d*), especially of the sulfids in nitric acid?

(*f*) Suppose a neutral solution[1] which contains compounds of all the metals that have been studied to be treated with hydrochloric acid or a soluble chlorid, like common salt (NaCl) according to the law of precipitation what will occur? Why? Add the reagent as long as any action occurs, and filter out the solid product. Of what compound is the precipitate composed?

Through this filtrate, which is now acid (HCl), pass hydrogen sulfid (H_2S) as long as any chemical change is produced. What is the product? How are the elements combined? Write the formulæ of the compounds.

Let this precipitate be filtered out, and the filtrate boiled until all of the dissolved hydrogen sulfid is expelled. To the clear filtrate add ammonium chlorid (NH_4Cl) and follow it by ammonium hydroxid (NH_4OH), adding enough of the latter

[1] By a neutral solution, as the term is used here, is meant one in which there is no free acid or free alkali. There are many salts that are acid or alkaline to litmus, as the case may be, but contain no free acid or alkali.

reagent to make the solution strongly alkaline. What reaction occurs? What is the precipitate, provided the iron is in the ferric condition in the solution?

Filter as before and add ammonium sulfid ($(NH_4)_2S_2$). Answer the questions just given. Suppose the ammonium sulfid had been added without filtering out the precipitate produced by ammonium hydroxid, of what would the precipitate have been composed?

To the filtrate from the ammonium sulfid precipitation add ammonium carbonate ($(NH_4)_2CO_3$). What is the precipitate produced? Filter and treat the filtrate with the reagent disodium hydrogen phosphate (Na_2HPO_4). Explain the result. The salts of what metals are left in this filtrate? The metals combined in these different precipitates constitute what are called the groups, and are numbered group I., II., III., IV., V. Magnesium stands by itself, owing to the use of ammonium hydroxid and chlorid in the third and fourth groups. (See under MAGNESIUM.) Group III. is sometimes spoken of in two groups, made by the reagents ammonium hydroxid and ammonium sulfid. The reagents used are called the group reagents, and will be so referred to hereafter.

(*g*) Suppose the mixture referred to in (*f*) were treated with a solution of sodium sulfate, what would occur?

(*h*) Using a solution of sodium carbonate on solution (*f*), of what would the precipitate consist? How could the remaining elements be removed, not including the alkali metals?

The separation and recognition of the members of these groups has been studied in the previous pages, and further, beginning on page 320. (The reactions that occur in the grouping should be written out, and those produced in the group separation and identification should be reviewed here.)

The Separation and Recognition of Acids. — The general principles made use of in the analysis of substances for bases

having been discussed, there remains to be treated those used in the analysis of substances for acids. The term *acid*, as used here, does not refer to the free acid, but means the acid corresponding to a salt. For example, it is common to speak of testing for sulfuric acid, when the meaning is to prove the presence or absence of a sulfate. Of course the tests given for the various acids in Part I. are used in testing for acids, whether free or combined.

The study of the acids will be facilitated if they are brought together and classified.

(*A*) According to their state of aggregation, including among the gaseous acids those that readily give gaseous products under conditions to be studied later on. A few organic acids are included in this list, the salts of which are often used in qualitative analysis. A few are included under two heads. Of course some of these acids do not exist except in the form of salts.

SOLIDS.	LIQUIDS.	GASES.
H_3PO_4	H_2SO_4	HCl
$H_2C_2O_4$	H_2SO_3	HBr
HIO_3	$HC_2H_3O_2$	HI
$H_2C_4H_4O_6$		HF
$H_3BO_3 - (B_2O_3)$		HNO_3
$H_3AsO_3 - (As_2O_3)$		HNO_2
$H_3AsO_4 - (As_2O_5)$		H_2S
H_2CrO_4 (CrO_3)	GASES.	(H_2SO_3)
H_4SiO_4 (SiO_2)	H_2SiF_6	$H_2S_2O_3$
$H_4Fe(CN)_6$	H_2CO_3	HClO
	$(H_4Fe(CN)_6)$	$HClO_3$
	$H_3Fe(CN)_6(?)$	(HIO_3)
	(HIO_3)	$(HC_2H_3O_2)$
	HCNS	HCN
		$HMnO_4$

In examining a solid substance, it is readily seen that (if acids are present at all) they must generally be combined with some base. (The exceptions are the few solid acids.) In this general discussion, the substance to be examined is understood to be in a solid condition, or in very concentrated solutions of their salts.

(*B*) *Classification of the Acids by Means of Sulfuric Acid.*

General Principle.—Sulfuric acid alone, or aided by heat, acting on solid salts, or on concentrated solutions of the salts, decomposes them, setting the corresponding acids free, or produces some characteristic products from these acids.

Those acids that are non-volatile, or that yield no gaseous products by this classification, will form a class by themselves, while all the others will constitute another class.

There are a few salts that correspond to volatile acids (in the sense just referred to) that are not readily decomposed, if at all, by sulfuric acid under the conditions named. These are the sulfids of arsenic, antimony, bismuth, and tin, and the chlorids of group I. The remaining sulfids of group II., and those of group I., are not very readily decomposed by sulfuric acid. Of course, the sulfates are not changed by this treatment.

This will arrange the acids in somewhat different classes[1] from those given in (*A*).

The "volatile" acids may be usefully classified into several groups by this same reagent.

(1) Those that have color or produce colored products. These are: HBr, HI, HClO, HIO_3, $HClO_3$, HNO_3, HNO_2, $HMnO_4$(?).

[1] It is not necessary to print these two classes, but the student should arrange them and determine what the products are in each case. For example, the sulfites are decomposed, forming sulfur dioxid (SO_2), water, and a sulfate of the metal of the sulfite. (See Part I. under each acid.)

(2) Those that are colorless and without odor. These are: H_2CO_3, $H_2C_2O_4$.

(3) Those that are colorless, but that possess a characteristic odor. These are: HCl, HF, H_2SO_3, $H_2S_2O_3$, $HC_2H_3O_2$, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, HCN, H_2S, H_2SiF_6.

(*C*) Hydrochloric acid decomposes the carbonates and most of the sulfids and sulfites. The sulfids require concentrated acid and the use of heat. Let us notice a single case out of many in which this general truth can be applied. Suppose that a mixture contains a carbonate and a chlorid, and that it is acted upon by sulfuric acid. As a result of the action two colorless gases escape, but one has an odor while the other is odorless. It is readily seen that the characteristeric product from the carbonate is masked by that from the chlorid. If the usual test for carbon dioxid is attempted, the halogen acid dissolves the calcium carbonate as it is formed. If, however, some of the solid mixture is now treated with hydrochloric acid, the carbonate alone is decomposed, and it is thus easily recognized. The fact of rapid effervescence and the odorless gas are sufficient to prove the presence of a carbonate. Examine the case of a chlorid and sulfite in the same manner.

(*D*) Another useful fact in the study of acids from this same general standpoint is the action of acetic acid on inorganic salts. It decomposes nearly all carbonates, but does not decompose oxalates and, in fact, very few of the other inorganic salts. How could this fact be used in distinguishing carbonates from oxalates, etc.?

(*E*) The acids are again grouped into two groups by the action of barium nitrate ($Ba(NO_3)_2$) (or barium chlorid ($BaCl_2$) may be used) upon neutral and not too dilute solutions of their salts. Or, in other words, into those that form soluble and those that form insoluble barium salts.

The groups are: —

Group I.	Group II.
H_2SO_4	HCl
H_2SiF_6	HBr
H_3PO_4	HI
$\left[\begin{matrix}HPO_3 \\ H_4P_2O_7\end{matrix}\right]$	HCN
H_3PO_3	$H_3Fe(CN)_6$
H_3BO_3	HCNS
$H_2C_2O_4$	$H_4Fe(CN)_6$
HF	H_2S
$H_2C_4H_4O_6$	HClO
H_2SO_3	$HClO_3$
$H_2S_2O_3$	$HClO_4$
H_2CO_3	HNO_3
H_2SiO_3	HNO_2
H_2CrO_4	$HC_2H_3O_2$
H_3AsO_3	$HMnO_4$
H_3AsO_4	$H_2S_2O_3$
HIO_3	

The barium salts of the acids of group I. are all dissolved by hydrochloric or nitric acids, except the sulfate and the rare fluosilicate. It is at once seen that a sulfate is recognized by this grouping. It may be well to note also that arsenous, arsenic, and chromic acids will be indicated in the separation of the metals. Again, many of the volatile acids of group I. may be removed by concentrated hydrochloric acid before making the test with barium nitrate.

(*F*) Silver nitrate forms a precipitate in neutral concentrated solutions of the salts of the acids in all cases except nitric, chloric, and acetic acids. Silver permanganate is sparingly soluble. If free nitric acid is present in the solution or is added to the precipitate, however, all of group I. (*E*) are

dissolved. This leaves the halogen acids HCN, $H_3Fe(CN)_6$, $H_4Fe(CN)_6$, and H_2S in the precipitate.

The uses of these facts in (*E*) and (*F*) are illustrated by answering the following questions: —

(1) Suppose silver nitrate is added to the neutral solution of a substance, and it produces no precipitate, what facts are established in reference to the presence or absence of salts?

(2) Suppose in (1) a precipitate is produced which is soluble in nitric acid; give the proper inference as in (1).

(3) Suppose neither reagent produces a precipitate, what are the conclusions?

(4) Barium nitrate produces a precipitate wholly soluble in nitric or hydrochloric acid. Explain.

The learner should understand that in many cases this grouping of the acids is only an aid in including or excluding certain acids from consideration for the particular substance under examination.

The test for individual acids already given and the conditions under which they can be applied will be given later on under their individual tests.

GROUP SEPARATIONS AND SOME SUGGESTIONS AS TO THE SOLUTION OF THE SUBSTANCE AND MANIPULATION.

Solution of Substances.[1] — Before any attempt is made to dissolve any given substance, it should be finely powdered. A small amount of the fine powder (100–200 mg.) is placed in a test-tube, and 10 cc. of pure (distilled) water is added, and the effect noted. It should always be heated after observing the effect of the cool water if solution is not effected. For example, does it dissolve, or is a new compound formed? That is, is there the formation of an oxy-salt as in the case of

[1] Review the paragraphs of the text referring to solution.

lead nitrate; or there may be a case which is illustrated by a mixture of sodium carbonate and barium chlorid. What oxy-salts may be formed?

It may be noted that one or more of four results will follow the addition of the water to the solid: (*a*) the substance wholly dissolves; (*b*) it does not dissolve at all; (*c*) it partly dissolves; (*d*) insoluble substances are formed through reaction with the water.

(*a*) If the substance wholly dissolves in water, sufficient (1 to 3 g.) for the group separation is put in solution, say in 30 to 50 cc. of water, and the work proceeded with as directed hereafter.

If (*b*), (*c*), or (*d*) results in most cases, the following treatment will generally be satisfactory. The undissolved solid is allowed to settle out, and as much as possible of the clear liquid turned off. HCl is now added drop by drop, and the whole heated, if necessary, to effect the solution. The same care as has been pointed out under (*a*) should be observed in noting the formation of new compounds, etc. Of course, (*a*) or (*b*) or (*c*) effects may result. If (*a*) results, then proceed as before directed in making the water solution, using the smallest amount possible of the HCl to effect the solution. See under group II.

Before using any other solvent, HCl should be tried from the dilute up to the concentrated acid, and the substance should be boiled in it, until it is determined that the substance is insoluble in this acid.

Most insoluble substances are soluble in this agent. Such substance as the compounds containing group I. bases, the sulfids of the second group bases (except antimony and tin, which are soluble in concentrated acid), are some of the exceptions. Others will be referred to under substances insoluble in ordinary solvent.

If, therefore, the substance is insoluble in HCl, a new supply of material may be examined with nitric acid, in the same way as before, and with the same possibilities as to solution.

Any substance which is insoluble in either HCl or HNO_3 should be filtered out and treated with aqua regia (two volumes of HCl to one volume of HNO_3).

Any substance that is not soluble in any of these reagents is likely to be the silver salts of the halogen acids, the insoluble sulfates, a few oxids like Al_2O_3, SnO_2, Cr_2O_3, minerals like the silicates, sulfur and carbon, SiO_2, some of the ferri- and ferrocyanids, etc.

Some of these substances may be indicated by examining the substances in the dry way on charcoal, as outlined under the "dry method." This is true of the lead, silver, and tin compounds. The metallic globule can be separated, dissolved, and the elements recognized in the usual way.

Another portion of the insoluble substance may be thoroughly mixed with Na_2CO_3 and fused. (On platinum foil in the absence of metals that alloy with it. Under these conditions fuse in porcelain crucible.) Suppose some one of the insoluble sulfates (*e.g.* $SrSO_4$) is present, the reaction is, —

$$SrSO_4 + Na_2CO_3 = SrCO_3 + Na_2SO_4.$$

The ordinary methods of solution and testing can now be applied. Of course the sulfate must be carefully removed before the carbonate is dissolved.

If a silicate (or SiO_2) is present (instead of $SrSO_4$, for example) when the water solution of the fused mass is made, and it is acidified with HCl, the SiO_2 is precipitated as a gelatinous mass, either directly, or after boiling for some time.

$PbCl_2$ and $PbSO_4$ are soluble in ammonium acetate. They are by this means separated from other insoluble substances. They may be recognized in this solution by H_2S, and the chlorid and sulfate by the usual tests. Also, the solubility of lead chlorid in hot water may be used to separate it. Silver chlorid is soluble in what? Set the silver free from all of the

halogen salts by zinc and dilute H_2SO_4. Where are the halogens? Test for them in the usual way.

In determining the presence of Al_2O_3 and Cr_2O_3, note the color of the substance. Test for Cr_2O_3 by usual fusion test. (See under CHROMIUM.) (Note the danger in the use of Pt. foil.) In the absence of colored substances make the cobalt test on charcoal. Fuse with $KHSO_4$, which forms a soluble compound containing the aluminium. Prove its presence in the usual way.

SnO_2 by itself may be recognized by its infusibility, by the fusion of an intimate mixture of the oxid with Na_2CO_3 and S. SnS is formed, which can be dissolved in $(NH_4)_2S_2$, and recognized in the usual way. It is separated in this manner from the insoluble salts of lead and silver.

Ferro- and ferri-cyanids are decomposed by sodium or potassium hydroxid. The hydroxid of the metal combined in the cyanid is separated and dissolved, and determined in the ordinary manner. The acid is left in solution as the alkali salt.

If the unknown solid substance requires HCl for its solution, care must be taken that it is not too acid before passing to the second group. (Of course the first group is absent under these conditions.)

The solution can be evaporated nearly to dryness, and then redissolved, or the acid may be, in part, neutralized by ammonia. It will be remembered that cadmium, antimony, and tin sulfids are soluble in fairly concentrated hydrochloric acid, and, therefore, would not be precipitated from a strongly acid (HCl) solution.

If there is a residue insoluble in HCl, or first group bases are present, and require HNO_3 for solution, the solution that goes to group II. must be evaporated to dryness (why?), and redissolved and acidulated with HCl. (In some cases the HNO_3 may be neutralized by ammonia, and the solution then acidified with HCl.)

The aqua regia solution must be evaporated to dryness, redissolved and acidified (HCl) before precipitating group II.

The conditions just described must obtain if the unknown substance is originally in solution. If the solution is alkaline when it is acidified, a precipitate may be formed which should be separated and examined in reference to its solution and determination according to previous directions. If a precipitate is formed under the conditions just given, by acidifying, the substances present are likely to be some of those treated under the head of insoluble substances, and, accordingly, it should be examined as directed for in the preceding paragraphs.

GENERAL DIRECTIONS FOR MANIPULATIONS IN GROUPING AND IN GROUP SEPARATIONS.

(*a*) The preliminary work in grouping should proceed thus: 5 to 10 cc. of the solution are treated with the group reagent, adding it drop by drop. Of course, one of two results will follow; namely, there is some of the group present, or there is none of it in the solution. If none of the first group is present, this same solution is treated with the second group reagent. If none of the second group is present, a new portion of the original solution is taken and treated with the third group reagents, and this solution is carried on to the fourth group if none of the preceding group is found. In every case all the group reagents must be added.

If any member (or members) of a given group is present, about 25 to 30 cc. of the proper solution is treated with the group reagent, and the precipitate is filtered out, and it is then ready for separation. The filtrate becomes the solution for the following group. The solution from group II. must be freed from H_2S before using it for group III. If iron is present, it must be oxidized before using the third group reagent. (Use HNO_3.) The original solution can be tested for iron, and its

condition determined. However, H_2S reduces ferric iron, and the filtrate from group II. will always contain the iron in the ferrous condition. In carrying out, in practice, the grouping of the elements, it is necessary to proceed in the order of the groups. All of each group must be removed before proceeding to the next. This is readily understood when a study is made of the facts upon which the grouping is based. These facts have been already examined. It is only necessary to note, for example, that the sulfids of the third group are insoluble in alkaline solutions, to comprehend why the second group bases should be removed before adding $(NH_4)_2S$, as directed in precipitating the third group. The learner should examine all of the groups in reference to this point.

STUDY OF THE GROUPS,[1] OR THE SEPARATION AND RECOGNITION OF THE BASES.

GROUP I.

Separation.

Precipitates ($AgCl$, $HgCl$, $PbCl_2$).—The precipitate is washed on the filter twice, with a little cold water. 20 cc. of boiling-hot water are now added to the precipitate, and allowed to pass through the filter. (It may be reheated and passed through again.) The lead is in the filtrate (No. 1) if present.

The precipitate remaining on the filter should be next washed twice, in boiling-hot water, to remove any traces of $PbCl_2$. NH_4OH is next added to the residue. The $AgCl$ is in the filtrate No. 2.

$HgCl$ is retained on the filter as NH_2HgCl, black, which is sufficiently characteristic.

See under LEAD and SILVER for their recognition in the filtrates Nos. 1 and 2.

[1] The student is familiar with these separations by his previous study, and the methods are brought together here as a matter of convenience.

Notes on Group I.

(1) A white precipitate on the first addition of HCl, but which dissolves on further addition of the acid, indicates antimony and bismuth salts in the solution. SbOCl and BiOCl are formed (see under these metals).

(2) A concentrated solution of $BaCl_2$ is precipitated by HCl.

(3) Note the crystals of $PbCl_2$ that form as the solution cools.

(4) Dry tests on charcoal are helpful in this work.

(5) Solutions of thiosulfates produce a white (yellowish white on boiling) precipitate when acidulated; SO_2 escapes, however.

(6) Alkaline solutions may give a white precipitate when acidulated. (See page 333.)

GROUP II.

Separation.

Precipitates (As_2S_3, Sb_2S_3, SnS (or SnS_2), HgS, PbS, CuS, Bi_2S_3, CdS). — These precipitates are washed and (*a*) the presence or absence of arsenic, antimony, or tin determined as follows. A little of the precipitate is transferred to a test-tube, and $(NH_4)_2S_2$ is added, and the whole gently heated. If it is all dissolved, only the sulfids of the elements mentioned are present. These elements constitute sub-group *A*.

If only a portion of the precipitate is dissolved, or it is uncertain whether any has been dissolved, the residue is filtered or the clear solution is turned off, and to it a few drops of dilute H_2SO_4 are added. If nothing is dissolved, the precipitate is white (sulfur), and none of sub-group *A* is present.

(*b*) If the precipitate by H_2SO_4 is colored, a sufficient amount of the original precipitate is treated with $(NH_4)_2S_2$, warmed, and the residue filtered out. This residue contains the sulfids of sub-group *B*.

Separation of Sub-Group A.

If none of sub-group *B* is present, the original group precipitate, containing sub-group *A* only, is therefore directly separated without first dissolving in $(NH_4)_2S$. In case sub-group *B* is proved to be present, then the precipitate in (*b*) is the one separated.

The precipitate is thoroughly washed, and the following preliminary examination made. If the precipitate is yellow, a little is placed in a test-tube, and $(NH_4)_2CO_3$ is added and warmed. As_2S_3 dissolves in this reagent, while Sb_2S_3 and SnS (or SnS_2) do not. (What conclusion?) Again, concentrated HCl completely dissolves the latter two sulfids, but does not affect As_2S_3. (Carefully distinguish free sulfur.)

Suppose (*a*) that all three of these elements are present.

The precipitate is boiled in concentrated HCl, and the residue is filtered out (it is $As_2S_3 + S$), filtrate No. 1. The residue is washed, and if it needs further recognition it is dissolved by $HCl + KClO_3$. The residue is transferred to an evaporating-dish, HCl added, and the whole heated, and small crystals of $KClO_3$ are added one at a time until the sulfid is dissolved. (Do not mistake sulfur here for undissolved As_2S_3; see note.) This solution is evaporated to dryness, care being taken that there is sufficient HCl to decompose all of the $KClO_3$. There must be no free chlorin. This solution contains the arsenic, and is used for its identification.

Filtrate No. 1 contains the antimony and tin compounds. They are separated by the Marsh generator. (See previous studies under ARSENIC and ANTIMONY.) Pass the gas into a solution of silver nitrate, thus leaving the tin in the generator, and the antimony is precipitated in the silver nitrate solution.

Identification.

Arsenic by Marsh's or by Fleitman's Tests. — Pass the gas into $AgNO_3$ solution. (See under ARSENIC.) The antimony is alloyed with the silver, and under these conditions is dissolved in HCl; and on filtering, the solution can be tested for antimony by H_2S and by H_2O, forming in this latter case SbOCl.

Antimony (see under ANTIMONY). — Some antimony is often left in the generator as a black residue, and must not be mistaken for tin.

Tin. — The tin is left in the generator, but is dissolved in HCl, while any antimony that may be left there, is not. Therefore, the liquid in the generator is filtered, the residue washed, and treated with hot HCl. The solution is tested with $HgCl_2$. (See under TIN.) The antimony residue may be dissolved and examined for that element. Nearly all zinc contains carbon, which may be mistaken for tin.

SUB-GROUP B.

Separation.

The thoroughly washed precipitate (or residue) (*a*) is treated with HNO_3 (use it as dilute as is possible) and boiled. (See notes.) Any insoluble black residue is HgS, which is thus separated from the other sulfids. The residue is filtered out (if the solution has not been made by pouring the hot acid on the precipitate without removing from the filter paper) and the *filtrate* is called *No.* 1.

(*b*) To 5 cc. of filtrate No. 1 add a few drops of dilute H_2SO_4; a precipitate indicates lead. (Note its presence in group I.) If lead is present, it is removed from 25 or 30 cc. of filtrate No. 1, and the precipitate filtered out. Lead (shown by group I. study or otherwise) may be removed by adding to 20 to 25 cc. of the solution a few drops of dilute sulfuric acid. Warm and allow to cool. Filter out the precipitate, $PbSO_4$.

(In some cases it is well to add about .25 to .5 cc. of H_2SO_4, and then evaporate the solution until fumes of SO_3 escape. Add a little water, cool, filter out the residue. The filtrate No. 2 is used for the other metals.) This usually sufficiently identifies the lead, especially if it has been found in group I. The precipitate $PbSO_4$ may be heated with 1 cc. of $K_2Cr_2O_7$ solution, and then washed, and KOH added, when a yellow solution is produced in confirmation.

(*c*) Filtrate No. 2, or No. 1 in absence of lead, is next made strongly alkaline with ammonia. Bismuth is precipitated as $Bi(OH)_3$. It is filtered out and washed. The filtrate No. 3 contains copper and cadmium.

(*d*) Copper and cadmium are separated by boiling filtrate No. 3 to expel excess of ammonia, slightly acidified with HCl, and adding (to a portion) of this solution $K_4Fe(CN)_6$. Copper forms $Cu_2Fe(CN)_6$ brown and insoluble. Into the other portion of filtrate No. 3 pass H_2S. (Be sure that the solution is only slightly acid.) CuS and CdS are precipitated. KCN dissolves CuS, but does not CdS.

Identification.

The HgS is identified by dissolving it in aqua regia, evaporating to dryness, redissolving in water, and making the usual test with $SnCl_2$.

Lead is sufficiently identified by separation and presence in group I.

Bismuth. — This metal is recognized by the solution of the hydroxid $Bi(OH)_3$ in dilute HCl, using only enough of the acid to just dissolve it. Examine portions of this solution with water, etc. (See under BISMUTH.)

Copper. — The production of the blue solution when filtrate No. 2 (or 1) is made alkaline by ammonia is considered satisfactory evidence of the presence of copper. Also the production of $Cu_2Fe(CN)_6$ is a delicate test for copper.

Cadmium. — In the absence of copper the yellow precipitate of CdS is characteristic. When copper is present, the treatment given in (*d*) is sufficient identification; *e.g.* the insoluble yellow residue after adding KCN to the mixed sulfids.

Notes and Questions on Group II.

(1) Remember that the solution from which the group is precipitated must not be too acid. Cadmium, antimony, and tin sulfids are soluble in concentrated HCl. Cadmium sulfid quite readily so.

(2) Note the color of the sulfids. In the absence of cadmium, what inference could be drawn from the fact that a given precipitate is yellow? or that it was wholly black?

(3) H_2S, acting on a soluble mercuric compound, at first may produce a white precipitate due to the formation of a compound of H_2S with the salt of mercury that may be present. For example, with $Hg(NO_3)_2$, the compound is $2\,H_2S.Hg(NO_3)_2$. The precipitate is finally decomposed, and black HgS is the product. The first precipitate often changes from white to light yellow, to darker shades, then to brown, and finally to black. This reaction is quite characteristic.

(4) HgS, when boiled for some time in HNO_3, often becomes white, owing to the formation of insoluble double compounds of variable composition. They are decomposed by aqua regia. SnS + Sb_2S_3 produce similar results if they are not removed by ammonium sulfid.

(5) Sub-group *A* may be separated from sub-group *B* by KOH, which dissolves the former sulfids. They can be reprecipitated from the filtrate by dilute H_2SO_4 (or HCl). They can then be separated and recognized as given in the separations.

(6) The AS_2S_3 which is dissolved and separated from the other members of sub-group *A* by $(NH_4)_2CO_3$ can be reprecipitated by acidifying, and the latter identified by heating the dry precipitate with Na_2CO_3 on charcoal. Garlic odor.

(7) CuS is partially dissolved in $(NH_4)_2S_2$, and therefore, if copper compounds are present, they are likely to be mistaken for tin in sub-group *A*. The presence of copper can generally be established before the group separation is made, and KOH or Na_2S_2 or K_2S_2 can be used to separate the two groups, since copper sulfid is not dissolved by these reagents.

(8) H_2S is a reducing agent for the third group bases, and consequently the presence of these metals in the condition of their higher oxidation causes its oxidation and the reduction of these elements. Ferric, chromic, and manganic compounds are reduced to their lower oxidation in the presence of HCl. Sulfur is, therefore, always precipitated when H_2S is passed into solutions containing these compounds. Are the precipitates of group II. white? The presence of these compounds can generally be inferred from the colors of the solutions. Write these reactions, using particular compounds, like K_2CrO_4, $K_2Cr_2O_7$, $KMnO_4$, etc. What effect might chlorates have under the conditions that obtain in group II. precipitation?

(9) If $(NH_4)_2S_2$ is used in this group, free sulfur is produced in several of the reactions. This may be further oxidized by aqua regia, forming sulfuric acid, which, in the presence of lead compounds with mercury, gives an insoluble white residue in the work with HgS.

(10) Arsenic compounds are always reduced to the arsenious form before the precipitation of As_2S_3. For complete precipitation of the arsenic, it requires the action of H_2S several hours, unless the arsenic is previously reduced by some other agent, like SO_2.

(11) Great care should be observed in testing for arsenic or antimony when they are combined as the hydrids AsH_3 or SbH_3, owing to the poisonous character of these compounds. The gases should be passed into a solution of silver nitrate, and the action not allowed to continue longer than is necessary.

(12) The sulfur set free in sub-group *B* by HNO_3, or by

aqua regia, may be slightly colored by the unchanged sulfids. Sulfur is also aggregated by boiling the solutions, and it is thus darkened in color. HNO_3, however, readily dissolves these sulfids without boiling.

(13) Platinum and gold sulfids belong to sub-group *A*. (See Prescott and Johnson's *Qualitative Analysis*, method of analysis.)

GROUP III.[1]

Separation — Sub-group A.

Precipitates: $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$. — This precipitate is thoroughly washed on the filter, and then rinsed by the reagent KOH into an evaporating-dish and boiled. Aluminium is dissolved as K_3AlO_3, while the other hydroxids are unchanged.

The residue containing the iron and chromium hydroxids is filtered out and washed. The filtrate is No. 1. No further separation is needed, since one base does not interfere with the tests for the other.

Identification.

Aluminium. — This element is recognized by acidifying filtrate No. 1, and adding ammonium hydroxid or $(NH_4)_2CO_3$. The gelatinous precipitate is characteristic. It may be examined by the dry method. (Cobalt, blue.)

Iron. — A portion of the residue insoluble in KOH is dissolved in HCl.KCNS, and other tests for iron are used to recognize it. Determine the state of oxidation of iron in the original solution.

Chromium. — Another portion of the precipitate is examined by the fusion test. (See under CHROMIUM.)

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[1] See notes 9 and 10.

Separation — Sub-group B.

Precipitates: MnS, CoS, NiS, ZnS. — This "sub-group" precipitate is carefully washed and treated on the filter, in the cold, with dilute HCl. (Cobalt and nickel sulfids are black, and this work is omitted unless one or both are present.)

This treatment divides the sub-group into two parts; the insoluble black CoS and NiS are left on the filter, and MnS and ZnS are in the filtrate, which is No. 1.

The separation of cobalt and nickel is somewhat difficult, and it is advisable to make the bead test (which see) first, and determine the necessity for separation. The absence or presence of cobalt, as determined by this test, decides whether a separation is necessary. (Note also the color of original solution.) The sulfids are transferred to an evaporating-dish, concentrated HCl added, and the whole is boiled. A small amount of HNO_3 may be added drop by drop until sulfids are dissolved. Concentrate the solution until the aqua regia is driven off, add a little water (must be concentrated solution, however), and follow with an excess of KCN. Boil the solution and add, while hot, NaClO. Or make the solution alkaline with NaOH (after adding KCN), and add bromin water to complete reaction. Warm gently, and let stand a few minutes. The cobalt is left in solution, and the nickel is precipitated as $Ni(OH)_3$ (see notes), and the separation is complete. Filter out the $Ni(OH)_3$, filtrate No. 2.

Filtrate No. 1 is treated with KOH, and only gently warmed (if at all). This reagent precipitates the manganese as $Mn(OH)_2$, and leaves the zinc in solution as K_2ZnO_2, filtrate No. 3.

Identification.

Cobalt. — Can always be identified by the bead test in filtrate No. 2.

Nickel. — The precipitate $Ni(OH)_3$ is thoroughly washed and identified by the bead test, by the color of its HCl solution, etc.

Manganese. — $MN(OH)_2$ is filtered out and washed and the fusion test made. (See under MANGANESE.)

Zinc. — To a portion of filtrate No. 3 add $(NH_4)_2S$. A dirty white precipitate is ZnS. Acidify another portion of the filtrate with $HC_2H_3O_2$, and pass in H_2S. ZnS is produced. (See under ZINC.)

Notes on Group III.

(1) The filtrate from group II. must be free from H_2S before the precipitation of sub-group *A*.

(2) After NH_4Cl and NH_4OH have been added (the latter in excess), the whole should be heated to precipitate the chromium.

(3) Only chromium in the basic condition is precipitated by ammonia. Solubility and color of solution and of salts will generally determine whether the chromates are present. Note that H_2S reduces the chromates in an acid solution. If, therefore, the indication mentioned in notes under group II. are found, it is often best to pass H_2S through the warm solution until the reduction is complete. However, soluble chromates are not precipitated by the group reagents, and do not interfere with the separation and recognition of the other metals.

(4) Manganates and permanganates are like the chromates, in reference to the action of H_2S, and also the group III., reagents. They may be reduced by H_2S. The reduction must be complete, and the solution must be boiled some time before the sulfur can be filtered out.

(5) Note that if NH_4OH produces no precipitate, sub-group *A* is absent. All similar facts should be at the command of the worker.

(6) *Manganese* is often found in sub-group *A*, since the hydroxid is not always completely dissolved by the reagents NH OH and NH_4Cl. It does not interfere with the usual

tests for these elements. It will also be found in sub-group *B*.

(7) *Nickel* sulfid is partially soluble in $(NH_4)_2S_2$, forming a brown solution. The filtrate should be warmed and *slightly* acidulated with HCl, when NiS will be reprecipitated.

(8) *NiS* and *CoS* are partially soluble in HCl, unless it is quite dilute and it is used in the cold. Therefore, the color of zinc sulfid is likely to be slightly affected by these sulfids. It will be noticed that the solution used in grouping is acid until group III. is reached, when it becomes alkaline.

(9) If the original substance requires an acid to dissolve it, and the acid (or acids) corresponding to the salts dissolved is not decomposed, then when the solution is made alkaline with ammonia, the compounds are reprecipitated, provided bases of group III. or IV. are present. Such salts are the phosphates, oxalates, fluorids, silicates, and borates.

The presence of NH_4Cl prevents the precipitations of the borates of group IV. and manganese oxalate.

The *phosphates* and *oxalates* are white, and consequently the appearance of the precipitate formed when the group II. filtrate is made alkaline is indicative of the presence of the salts of some one or more of these bases. The original substance should be examined for these acids. If the substance is a solid, it should be dissolved in nitric acid and the solution tested for phosphoric acid. If oxalates are suspected, they may be decomposed by a little sulfuric acid, heating to aid the decomposition, and the residue dissolved and analyzed in the usual manner. Or the oxalate may be decomposed by heat (red heat), and the residue dissolved and analyzed as before.

If *phosphates* are present, it is perhaps better to remove the acid before proceeding to the analysis of these two groups.

In this case make the complete precipitation by the sub-group *A* reagents (group III.), and filter and carefully wash the precipitate. (The filtrate may be tested for fourth-group

bases and magnesium.) The washed precipitate is transferred to a beaker, and concentrated HNO_3 added along with metallic tin. (Sufficient tin must be added to precipitate all the phosphoric acid combined with tin, as $Sn_3(PO_4)_4$.) The phosphate is filtered out, the filtrate diluted, and examined for the bases of the two groups. (It may be added to the filtrate from the first precipitation.) Another satisfactory method consists in removing the phosphate by means of $FeCl_3$. To the acid (HCl) solutions ammonium acetate is added, until all of the free HCl is neutralized, and then $FeCl_3$ is added as long as any precipitate is formed. The phosphoric acid is thus removed as ferric phosphate ($FePO_4$). The filtrate is now examined for the bases of groups III. and IV. Iron must be tested for in the original solution.

Fluorids, if found to be present, should be decomposed by H_2SO_4.

Magnesium borate may be decomposed by H_2SO_4, and magnesium identified in the usual manner. The other borates are kept in solution by NH_4Cl.

(10) All of the members of group III. may be precipitated together on adding the two group reagents at once, and the separation made afterwards. It is not necessary to oxidize the iron under these conditions, and H_2S is not necessarily expelled before precipitation. (Why?) The learner can develop a method. Suppose dilute HCl is added to the precipitate, what occurs? Add NaOH in excess and boil; what will the precipitate contain?

(11) The separation of nickel and cobalt can be made very satisfactorily by the following method. The concentrated solution of the chlorids, as prepared in the regular group separation, is neutralized by NaOH, adding it until a small permanent precipitate is formed. Acetic acid is next added, until this precipitate is dissolved, when a concentrated solution of KNO_2 (or a piece of the solid salt) is added. The mixture

should stand for at least 12 hours. The yellow precipitate that is formed is $3\ KNO_2.Co(NO_2)_3$. The reaction is,—

$$CoCl_2 + 2\ HC_2H_3O_2 + 7\ KNO_2 = 3\ KNO_2.Co(NO_2)_3 + H_2O + NO + 2\ KC_2H_3O_2 + 2\ KCl.$$

The nickel is left in solution, and should be tested for by adding NaOH to the filtrate to alkaline reaction. The precipitate is examined by the bead test.

GROUP IV.

Separation.

Precipitates: $BaCO_3$, $SrCO_3$, $CaCO_3$. — The group precipitate is washed, and dissolved in acetic acid. (May be done on the filter, warming the acid.) To 5 cc. of this acid solution add $K_2Cr_2O_7$, and warm. A yellow precipitate is $BaCrO_4$. If therefore barium is present, a sufficient amount of solution is used, and barium is separated as $BaCrO_4$. This precipitate is separated by filtration, and filtrate No. 1 contains strontium and calcium compounds and the excess of $K_2Cr_2O_7$.

Filtrate No. 1 is now treated with NH_4OH (to alkalinity), and $(NH_4)_2CO_3$ is added to complete precipitation. The precipitate is filtered out and washed until the yellow solution is removed. This precipitate is again dissolved by acetic acid (on filter), and the filtrate or solution contains the acetates of the two metals. Filtrate or solution No. 2. These metals are separated from filtrate No. 2, as follows: The solution is divided into two parts. One of these portions is treated with a saturated solution of $CaSO_4$, and thoroughly shaken, heated, and allowed to stand for a few minutes. Strontium is present if a white precipitate forms. Under these conditions add $(NH_4)_2SO_4$ to the second portion, and boil. The strontium sulfate (see page 322 for solubility of) is precipitated and is filtered out, and the calcium is left in solution. ($CaSO_4$ is soluble in $(NH_4)_2SO_4$.) Filtrate No. 3. This filtrate (No. 3) contains the calcium.

Identification.

Barium. — This element is sufficiently identified by the yellow $BaCrO_4$ and the flame test. Some of the yellow precipitate is washed and dissolved in HCl, and the solution used for the flame test. ($BaCO_3$ can be used provided the other two bases are absent.)

Strontium. — This element is identified by the facts learned in its separation in connection with the flame test. The sulfate may be used as was $BaCrO_4$ for barium. The fact of precipitation by $CaSO_4$, if barium has been wholly removed, is sufficient evidence of the presence of strontium.

Calcium. — Filtrate No. 3 is treated with $(NH_4)_2C_2O_4$, and the formation of a white precipitate, in the absence of Sr and Ba, is a delicate test for calcium. CaC_2O_4 is insoluble in water (1 to 500,000), but is insoluble in dilute acetic acid. The same salts of barium or calcium are soluble in acetic acid.

Magnesium. — The filtrate from group IV. contains magnesium, since its chlorid and sulfid are soluble in water, and its hydroxid and carbonate are soluble in NH_4Cl.

Magnesium ammonium phosphate ($Mg(NH_4)PO_4$) and magnesium hydrogen phosphate ($MgHPO_4$) are insoluble. The solution should be fairly concentrated, and this filtrate may be concentrated before making the usual test. (Filter if not clear.) To the solution add Na_2HPO_4, or better, $NaNH_4HPO_4$, stirring the solution and rubbing the sides of the beaker or test-tube with a glass rod.

A crystalline precipitate is considered satisfactory evidence of the presence of magnesium. The crystalline character of the precipitate becomes more evident on standing for some time. (NH_4OH and NH_4Cl must be present.)

A precipitate is sometimes formed which is due to the imperfect removal of the group IV. bases, and sometimes aluminium is carried over from group III. and is precipitated as aluminium

phosphate ($AlPO_4$). This precipitate is always small in quantity, and is never crystalline. It is insoluble in acetic acid. $MgNH_4PO_4$ is soluble. Traces of group IV. bases may be removed by use of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$.

Notes on Group IV.

(1) The flame tests for group IV. bases can be made with the original substance by adding HCl to some of the solid (or to the concentrated solution) and dipping the wire in this solution, providing no first or second group bases are present to form fusible alloys with the platinum wire. A portion of the group precipitate dissolved in HCl gives better satisfaction, especially when only one member is present.

(2) $K_2Cr_2O_7$ precipitates $BaCrO_4$ from acetic acid solutions, while calcium and strontium are not so precipitated.

(3) $CaSO_4$ may be used to determine whether barium or strontium are present in the acetic acid solution of the group precipitation. If barium is present, this reagent produces a precipitate on its addition, while strontium sulfate forms slowly, and, of course, calcium can produce no precipitate.

Strontium sulfate being more soluble than barium sulfate will produce a precipitate of $BaSO_4$ in solutions of barium salts. It could form no precipitate in solutions of calcium or its own salts, and hence may be used to distinguish barium in presence of either one or both of these bases.

GROUP V.

Group V. is sometimes made to contain magnesium, potassium, sodium, and ammonium. Magnesium stands between this group and group IV. From the ordinary standpoint of grouping, — namely, that of precipitation with other bases in some common form, — it is not included in any group. It, however, is not a vital question, and it is left between the groups IV. and V.

The other elements are brought together here since they are left in the solution by the group reagents. All of their common salts are quite soluble in water, and there is no common salt that is not partially soluble. The double salt of potassium platinum chlorid ($2KCl.PtCl_4$ and ammonium platinum chlorid $2NH_4Cl.PtCl_4$) are quite insoluble. The former salt is especially so in mixtures of alcohol and water. The corresponding sodium salt is quite soluble. Sodium can be separated from potassium, therefore, since the regular scheme of separation has left only these bases in the final solution. This solution is evaporated to dryness and heated sufficiently to decompose the ammonium salts. This residue is now dissolved in the smallest amount of water possible and treated with the reagent, $PtCl_4$. If potassium compounds are present, a yellow crystalline precipitate is formed. (Alcohol aids in this precipitation.)

Flame tests are, however, usually satisfactory. (See page 299.) The original solid (or residue from evaporation of the solution) is treated with HCl and the tests made as directed. Bases of the first two groups interfere with the use of the platinum wire, as has already been explained. If present, they may be removed by H_2S and the solution evaporated. Iron wire may take the place of the platinum wire also. The blue glass must be thick enough to cut off all but the violet rays. (Two or three pieces may be necessary.)

Sodium can always be identified by the flame test.

Ammonium should always be tested for in the original solid or in the concentrated solution, as directed under ammonium.

RECOGNITION OF THE ACIDS.

The general principles, or facts, in reference to the analysis for acids have been given on page 324 (which see). It is there learned that the acids cannot be grouped and separated as readily as are the bases. However, the application of these principles renders their determination, in most cases, less difficult than the determination of the bases.

In general, the substance to be examined is to be in the solid form, either originally, or it has been made so by the evaporation of its solution. Of course, in many of the tests, the substance is in solution, but the preliminary examination always requires the condition just given.

The facts to be used in the determination of the acids are the following, and they should be learned in the order stated: —

(*a*) The bases that are present in the unknown substance. Consequently, the bases should be determined first.

(*b*) The solid substance is treated with H_2SO_4, according to the method suggested under the consideration of the general principles, page 326.

(*c*) The knowledge that is gained by the use of the reagents $BaCl_2$ and $AgNO_3$.

(*d*) Individual tests combined with a knowledge of what acid and bases will interfere with these tests.

(*e*) Facts derived from the solution of the substance.

(*a*) The use of (*a*) is best seen by a few illustrations. Suppose that an unknown substance contains lead and barium as determined by the group work. Now combine these facts with the fact that the substance was soluble in water, and what can be said about the presence or absence of acids? It is readily seen that there could be no sulfates, carbonates, phosphates, etc., present. In fact, an examination of the list of acids taken in connection with the solubility of salts shows that only acetic, nitric, and chloric acids could be present under

the conditions. These acids are, therefore, the only ones for which an examination is made.

The use of the facts of solubility can be further illustrated by a few questions: —

(1) The substance is soluble in water, and iron and aluminium are present; what acids are excluded?

(2) The same conditions of solubility as in (1), and silver, zinc, and potassium are present; what acids are absent?

(3) The substance requires HCl for its solution; what acids are absent?

(4) The substance is soluble in water, and sodium, potassium, and ammonium are present; what can be decided about the acids possibly present?

(5) The substance is wholly insoluble in the usual solvents; what acids may be present?

(*b*) In applying (*b*), about two grammes of the substance is placed in a dry test-tube, and enough H_2SO_4 is added to cover it. The effect of the acid in the cold is carefully noted, shaking the tube so as to bring the acid in contact with all of the solid. The odor, color, etc., of any escaping gas is noted and studied in the light of the classification given on page 326.

The substance is next gently heated, care being taken not to vaporize the H_2SO_4 (338°). The same observations as before must be made. (It may be remarked here that the worker must know how different acids (salts) act under these conditions. He has already learned this in Part I. and on page 324, where the general principles have been discussed.)

The most characteristic result of this treatment is perhaps that in which no volatile products are formed, and the acids present are included in the non-volatile list. These are often so closely determined by the examination for bases and by solubility that only one or two acids must be looked for. (See under individual tests for acids.)

If volatile acids are present, the facts and classification on

page 326 and the use of HCl and $HC_2H_3O_2$ should be employed, but do not need further application here.

(*c*) Negative results with these two reagents, $Ba(NO_3)_2$ and $AgNO_3$, are the broadest in their conclusions as to the presence or absence of acids. In case both reagents give no precipitate, only three acids are generally tested for. (See page 327.) In the absence of fluosilicic acid, the use of $Ba(NO_3)_2$ gives a characteristic and definite result for sulfuric acid. $AgNO_3$ is equally definite for each of the halogen acids. With the facts given under the general principles the student must gain facility in their use by application to the cases as they come up.

Having derived the knowledge that can be gained by applying (*a*), (*b*), (*c*), the confirmation tests (when needed) are made with the individual acids. These tests have been already studied in most cases, and will be referred to in such a manner that the student can apply the test without further description. It is always understood that the tests in Part I. are indicated.

(*d*) The individual tests for acids will be studied from two standpoints; namely, the possible interference of the bases and of the other acids with the usual tests.

Most of the usual tests for acids are applied in the wet way, and therefore the question of solubility of the salts is an important consideration. For example, the student must decide what acids he can expect in the water solution and what ones in the acid solutions. He has only to examine the solubilities to answer such questions as the following, always with the understanding that the substance is already in solution in water or that the solid substance has been treated with water. Where will the nitrates and acetates always be found? Where are the chlorids in the absence of group I. bases? If insoluble phosphates, and some of the chlorids, and nitrates are present, how could they be separated for testing? Bases may be removed from these solutions by Na_2CO_3.

The acids are taken up in alphabetical order.

Acetic Acid. — This is an organic acid, and methods for its recognition have been given. Its salts are decomposed by sulfuric acid, and the gas escapes at 119°. The following test is not interfered with by bases. To the solid substance in a test-tube sulfuric acid and alcohol are added, and the whole is warmed, when there is formed a compound possessing an agreeable odor. The compound is ethyl acetate. Other alcohols may be used, each producing a compound possessing a characteristic odor. (Like all odors, this must be experienced before it can be recognized.) Other odorous volatile acids will interfere with this test. Since the acetates are always in the water solution under such conditions, a concentrated (strictly neutral) solution may be treated with $FeCl_3$, and boiled. ($HgCl_2$ must be absent.) Acetates produce a red solution which deposits a brown basic iron acetate on boiling. When the dry acetate is heated to a high temperature, it is decomposed, and acetone is driven off. This gas has an agreeable ethereal odor and burns when inflamed.

Arsenous Acid. — This acid is always determined with the bases. Arsenites give some characteristic precipitates. (See under this topic.)

Arsenic Acid. — Arsenates are slowly decomposed by H_2S, and arsenous sulfid (As_2S_3) is formed. This fact indicates in which condition the arsenic is, in the original substance. Soluble arsenates produce characteristic precipitates with $AgNO_3$ and with the reagent ammonium molybdate. (See under phosphoric acid for the interference with the latter test.)

Boric Acid. — Boric acid is tested for by the flame test, *i.e.* alcohol and sulfuric acid (or glycerine on platinum wire) acting on the solid substance. The bases copper and barium may interfere with this test. If, therefore, one or both are present, they should be removed by Na_2CO_3, the solution concentrated, and the flame test made. The rare elements, tellurium, thallium, and molybdenum, also color this flame green.

Phosphoric acid sometimes imparts a faintly bluish-green color to the alcohol flame. There is rarely any difficulty with this acid.

Chromic Acid. — The solubility of these salts and the color of the solutions are good indicators of chromates. Again, in the precipitation of group II. the precipitation of sulfur and change in the color of the solution afford good evidence of the chromates. In case of soluble chromates, the precipitates produced by $Pb(C_2H_3O_2)_2$, $Ba(NO_3)_2$, and $AgNO_3$ are also quite distinctive. When reduced, the chromates give chromium in group III. analysis.

Carbonic Acid. — This is a volatile acid, and, therefore, bases that may be present do not interfere. Bismuth carbonate is only slowly decomposed by H_2SO_4. It is more rapidly decomposed by HCl (dilute or concentrated). Several of the volatile acids interfere with the H_2SO_4 test for carbonates. They can practically all be eliminated by the use of HCl or of acetic acid or of both of them. For illustration, see page 327. The product CO_2 may be passed into $Ca(OH)_2$ or $Ba(OH)_2$ for further evidence.

Chloric Acid. — Chlorates are decomposed by H_2SO_4, giving free chlorin; and the sharp detonations, especially when slightly heated, are characteristic. (See page 287, Part I.) Chlorids in presence of certain powerful oxidizers (MnO_2) give free chlorin when heated with H_2SO_4, but the action is not accompanied by explosions. Chlorates when heated give off oxygen and deflagrate when heated on charcoal. (Nitrates and nitrite also deflagrate.) Iodin will set chlorin free from chlorates.

Ferro- and Ferricyanic Acids. — Most of the salts of these acids are insoluble in water, and many of them are insoluble in water and acids. (See under insoluble substances for their insoluble salts.) The other soluble salts of these acids are decomposed by H_2SO_4, and HCN is set free. This gas has a characteristic odor resembling that of peach blossoms. (It is, however, very poisonous, and should not be inhaled.) The

soluble salts (in water or in acid) are recognized by the action of the salts of iron. It will be remembered that iron is identified in soluble compounds by the action of the alkali salts of these acids. Of course the test can be reversed. Also note the grouping by means of $AgNO_3$. This reagent produces an orange-colored precipitate with ferricyanids, and a white precipitate with ferrocyanids (dilute HNO_3 solution).

The alkali ferrocyanids are insoluble in alcohol, while the corresponding ferricyanids are soluble. The insoluble salts of both of these acids are decomposed by the fixed alkalis, and after filtering out the insoluble hydroxid, the filtrate can be tested for the acids. Use alcohol for separation.

Fluosilicic Acid. — The salts of this acid are rare, and are decomposed by H_2SO_4, HF being set free. (See FLUORIDS.) This serves as a distinction from sulfates, the only acids for which it is likely to be mistaken. Its precipitate with $Ba(NO_3)_2$ is insoluble in acids. (See under H_2SO_4.)

Hydrogen Chlorid. — The usual examination of the solid with H_2SO_4 is sufficiently characteristic to recognize this volatile acid, except in the presence of the other halogen acids. (See under SEPARATION OF.) The indications by the use of sulfuric acid may be confirmed by moistening a glass rod in a solution of $AgNO_3$ and holding it in the escaping gas. The precipitate formed on the rod should be rinsed into a test-tube with a little water and treated with ammonium hydroxid. In other words, the precipitate must be shown to possess the properties of AgCl. HCN gives a precipitate, AgCN, that has about the same solubility as AgCl. (See under HCN for distinction.) The $AgNO_3$ test in water solutions should be used to confirm the other tests. The other acids of the silver nitrate group, of course, interfere. The chlorates interfere with the H_2SO_4 test for the chlorids. This difficulty may be overcome by remembering that HCl decomposes chlorates, but cannot change chlorids. Also the insoluble and soluble chlorids may be separated

($AgNO_3$), since the chlorates are all soluble in water. The soluble chlorids may be recognized in the presence of the chlorates by means of silver nitrate, since silver chlorate is soluble. In the presence of other members of the $AgNO_3$ group, this precipitate may be examined for the halogens.

Bases, of course, cannot interfere with these tests. The insoluble chlorids are recognized under insoluble substances, page 331.

Hydrogen Bromid. — Bromids are readily decomposed by H_2SO_4, except those of the first group bases, and the tests are only interfered with by nitrates and nitrites, which give a brown gas, NO_2, when decomposed. These are the only acids that produce a brown gas. Iodids may somewhat mask the brown color. (See SEPARATION OF BROMIDS FROM IODIDS.) $AgNO_3$ produces a precipitate in the water (or HNO_3) solution, which is slightly yellow, and is only partially soluble in NH_4OH.

The *bromids* are usually in the water solution, and the carbon disulfid test is thoroughly characteristic in the absence of iodids. (See SEPARATION; and page 37, Part I.) It should be noted that bromids, when decomposed by hot H_2SO_4, reduce this acid, setting SO_2 free. Iodids have the same effect. The insoluble bromids are recognized by the same method as is employed for the chlorid or iodid; namely, the bromid is decomposed by zinc and H_2SO_4, and the bromin tested for in the solution in the usual manner.

Hydrogen Iodid. — The same facts, in general, that were true for hydrogen bromid are true for hydrogen iodid. The result with H_2SO_4 and the carbon disulfid test are sufficiently characteristic in the absence of the bromids. (See page 41, Part I., and also below.) Note the effect of iodids on H_2SO_4.

Separation of the Halogen Acids (except HF). — The exception in reference to the insoluble salts of group I. bases should be noted for all of these acids. The student can develop a method for the separation of these salts. For example, AgCl is soluble

in what? $PbCl_2$ in what? etc. Perhaps the best method is to fuse the insoluble salts on charcoal with Na_2CO_3, and then dissolve the residue and examine the clear solution for the halogens.

The combinations that are possible in reference to these three salts are: —

(*a*) An iodid and a bromid.

(*b*) An iodid and a chlorid.

(*c*) A bromid and a chlorid.

(*d*) All three salts together.

All of these salts are to be in solution.

For (*a*), apply the facts demonstrated on page 44 (3 and 4), Part I.

(*b*) Of several methods for this separation, perhaps the best one depends on the fact that HNO_3 (sp. gr. 1.4) decomposes iodids and bromids, setting both iodin and bromin free.

A somewhat dilute solution of (*b*) is made, and nitric acid added, a few drops at a time, and the whole heated until all of the iodin is set free; *i.e.* until the solution becomes nearly colorless. This solution is now examined for a chlorid by silver nitrate. The precipitate must give the tests for silver chlorid.

(*c*) Proceed in the same manner as with (*b*). The bromin must all be set free. The solution should not be too concentrated.

(*d*) Both *iodin* and *bromin* having been proved to be present by the chlorin and the CS_2 test (*a*), a new solution is treated with nitric acid and heated until all of these elements have been driven off. This clear solution is examined for a chlorid as before.

Hydrogen Fluorid.—This is the only gaseous compound set free by H_2SO_4 that will corrode or etch glass. Its odor is also suggestive. If the presence of a fluorid is suspected, the solid substance is placed in a lead dish, H_2SO_4 added, and the dish covered by a piece of glass. (See page 51, Part I.)

Hypochlorous Acid. — The hypochlorites are all soluble in water, and hence are always found in the water solution of substances. The H_2SO_4 test is usually satisfactory for this acid. The result of this treatment is the sudden and rapid formation of free chlorin, which is not accompanied by explosions. (See CHLORID, AND AN OXIDIZING AGENT.)

None of the salts of other acids will interfere with this test. The result may be confirmed by the property of oxidation possessed by all hypochlorites. For example, the water solution of these salts oxidizes manganese (Mn^{II}) to (Mn^{IV}). Manganese chlorid ($MnCl_2$) becomes MnO_2.

Hydrogen Sulfid. — Sulfids are generally readily decomposed by hot sulfuric acid. Exceptions have been noted on page 326. Concentrated HCl decomposes most of these that are not decomposed by H_2SO_4. The prominent exceptions for both acids are HgS and As_2S_3. These substances may be dissolved in nitric acid or in aqua regia, and the presence of sulfuric acid in the solution determines that the original substance was a sulfid. (Insoluble sulfates are white.) Sulfur is also set free from sulfids by the latter two reagents.

This acid being a gas, the recognition is not interfered with by other acids nor by bases, with the exceptions noted. The odor test and the action of the acid on lead acetate (paper) are sufficient for its recognition.

Hydrogen Cyanid. — The cyanids are all decomposed by H_2SO_4, and the odor test is usually sufficient for their identification. In the absence of chlorids, the silver nitrate test (using the glass rod) is satisfactory. The AgCN is not as readily soluble in NH_4OH as is AgCl. In case HCl (or the halogen acid salts, in general) is present, and the substance is soluble in water, make the solution alkaline with NaOH, and add a mixture of a solution of a ferrous and ferric salt ($FeCl_3$ and $FeSO_4$), and warm. Next acidulate the solution with HCl, when, if a cyanid is present, prussian blue is precipitated.

If the cyanid was insoluble (and in the presence of chlorids), it may be decomposed by concentrated HCl, and the gas passed into NaOH (somewhat dilute), and the solution tested by the test just given.

Iodic Acid. — The iodates are generally insoluble except those of group V. bases. Sulfuric acid transposes all of the iodates. Those of group I. are, however, best transposed by HNO_3. No free iodin is formed, however, short of a temperature of 300°, unless some reducing agent, like SO_2, is present. The presence of the iodids and bromids can be determined by means of chlorin and CS_2. The iodids and bromids can be decomposed by HNO_3, and the gases driven off. The iodate is left undecomposed, and may now be decomposed by H_2SO_4 and some reducing agent, or the iodin may be freed by SO_2. (See under SO_2.) Iodates are decomposed by nitrous acid. They are recognized by treating the solution of the iodate with $NaNO_2$ and adding a little acetic acid. The test may be reversed for nitrites.

Nitric Acid. — The nitrates are all soluble in water, and freely so, except those that form oxy-salts. These latter salts are sufficiently soluble to permit the recognition of the acids in this solution. The brown ring test can always be applied under conditions given below. H_2SO_4 decomposes all of the nitrates, and the brown gas, NO_2, is usually formed in sufficient amount to indicate the presence of nitrates. In case of a small quantity of the nitrate, however, the fumes are not always evident.

Bases that form precipitates with H_2SO_4 or with sulfates interfere with the test. These bases must be removed before the test is made. If they are precipitated by Na_2CO_3, the excess of carbonate must be neutralized by $HC_2H_3O_2$. The solution of $FeSO_4$ must be fairly concentrated and must not be already oxidized. Neither the solution to be tested nor the H_2SO_4 and $FeSO_4$ can be more than warm when the test is made.

The acids that interfere with this test (and that with H_2SO_4, also) are the nitrites, iodids, bromids, and chlorates (iodates), and all acids that give a brown gas when decomposed by H_2SO_4.

The iodids and bromids can be removed by chlorin, heating until the excess of chlorin is removed. The solution is cooled and tested by the "brown ring test." (See under NITRITES; and also page 255, Part I.) The iodids and bromids may be removed by Ag_2SO_4. The chlorates may be removed by gently heating the dry substance until the former are decomposed; the residue may be tested for the nitrates. Concentrated HCl also decomposes them. The iodates may be reduced by SO_2, and the iodin further freed by chlorin.

Nitrites. — The nitrites are all soluble in water except that of silver, which is sparingly soluble. Nitrites give results in most cases like those produced by the nitrates. The two compounds can be distinguished, however, by methods given on page 256. The most difficult recognition is that of a nitrate in the presence of a nitrite. The difficulty is, however, with the nitrate; *i.e.* if a nitrite is found to be present, the recognition of the nitrate becomes one of some difficulty. The details of the method for this separation will not be given. Generally speaking, however, the nitrite can be removed by reducing the nitrite by KI, acetic acid being present, and driving off the products. The nitrate is left unchanged.

Oxalic Acid. — The oxalates, except those of the alkaline bases, are generally insoluble in water, but are soluble in acids. H_2SO_4 decomposes the oxalates, setting CO_2 and CO free in equal volumes. The free acid is a solid and is decomposed by H_2SO_4, producing the same products as it does with its salts. The oxalates of group IV. are transposed by boiling with a solution of sodium or potassium carbonate, so that sodium or potassium oxalate is in solution, and the metals of the oxalates are combined as carbonates and are separated

by filtration. The excess of Na_2CO_3 can be neutralized by $HC_2H_3O_2$, and the solution examined for the acid by a solution of calcium chlorid ($CaCl_2$), which forms a precipitate in this acid solution. Sulfates must be absent.

The same test can be applied to water-soluble oxalates with the exception noted. In case of the presence of sulfates, they are removed from the solution by adding HCl and then $Ba(NO_3)_2$, being careful not to add a large excess of the precipitant. The $BaSO_4$ is filtered out, and the solution is neutralized by NH_4OH. The excess of $Ba(NO_3)_2$ will be precipitated as BaC_2O_4, but the solution will generally contain sufficient of the oxalic acid for the usual testing. In case of a small amount of an oxalate the acid may be found in the precipitate BaC_2O_4. As with all acids producing gaseous products, the action of sulfuric acid on the dry solid is the starting-point in examining for this acid. If much gas is given off, it may be collected (or ignited at the mouth of the tube), and its "burning" taken as proof of its origin from an oxalate. The effervescence with H_2SO_4 is usually much less rapid than it is with carbonates. Oxalates do not effervesce with $HC_2H_3O_2$. By a combination of the facts just given, the oxalates can be readily recognized.

Phosphoric Acid. — The full metallic phosphates and those of the form M_2HPO_4 are all insoluble in water except those of the alkali bases. They are, however, all soluble in acids. The phosphates of the form MH_2PO_4 are generally soluble. For example, $CaHPO_4$ and $Ca_3(PO_4)_2$ are insoluble, while $CaH_4(PO_4)_2$ is soluble. The latter phosphates are not often met with.

The characteristic test for phosphoric acid is the yellow precipitate produced by the nitric acid solution of ammonium molybdate. (See page 265, Part I.) The way the precipitate forms and the changes produced as the solution is warmed are quite characteristic.

The soluble phosphates can be tested for in the solution

without interference from bases or acids with the exception to be noted. However, reducing agents interfere with this test because of their action on the reagent. They can generally be removed or oxidized by nitric acid before the addition of the test solution. (Reducing agents generally produce blue solutions and precipitates, sometimes brown.)

The insoluble phosphates should be dissolved in nitric acid, so that reducing substances will generally be oxidized. Arsenic acid and arsenates produce a yellow precipitate under the conditions indicated for phosphoric acid. Therefore if phosphoric acid is indicated by solution and the work on the bases and also arsenates, the latter should be reduced and removed by H_2S before the test is applied. In applying the test, the best results are reached when 5 to 10 cc. of the reagent are placed in a test-tube, warmed, and the solution to be tested added slowly to this. (See under BORIC ACID.)

Permanganic Acid. — The salts of this acid are colored, mostly red or purple, and are all soluble in water. Silver permanganate is sparingly soluble. The presence of permanganates is indicated by the color of the water solution, by the action of H_2S in the precipitation of group II., also by the purple gas that is (often) driven off when the solid salts are treated with H_2SO_4. The permanganates are powerful oxidizers, and consequently when heated on charcoal they deflagrate.

If the permanganates are heated with concentrated HCl, they are reduced, and the manganese is found in the solution as $MnCl_2$. How could manganese in the basic condition be recognized?

Sulfurous Acid. — The sulfites are generally insoluble in water, except those of group V. They are dissolved or decomposed by acids. In general, the sulfuric acid test is characteristic; that is, the odor is very distinctive. The SO_2 which is set free may be passed into a solution of an iodate in a slightly acid solution. (See page 210, Part I.) Another delicate

test, in the absence of sulfids, is made by reducing the sulfite by means of nascent hydrogen. The sulfur is reduced to H_2S, which is recognized in the usual manner by lead acetate. If a sulfid is present, it can be removed from the acetic acid solution by a solution of $ZnSO_4$, or from its HCl solution by a solution of some group II. base. Note that some reducing agents form SO_2 in the H_2SO_4 test.

Sulfuric Acid. — The insoluble sulfates are recognized by methods already given (see page 331). In the absence of fluosilicic acid and its salts, the usual test for this acid is not interfered with, either by bases or by acids. With the exceptions noted, the sulfates are always in the water solution, and, therefore, are readily tested for. If $BaCl_2$ is used instead of $Ba(NO_3)_2$, first group bases must be absent. In presence of fluosilicates this acid can be recognized by first removing the fluosilicates by the action of NH_4OH which decompose these salts, precipitating SiO_2.

Sulfocyanic Acid. — Sulfocyanids are decomposed by H_2SO_4, and HCN is given off. Most of the sulfocyanites are soluble in water. The salts of silver, lead, and mercury (-ic) constitute the principal insoluble ones. The characteristic test for this acid is the action of a ferric salt ($FeCl_3$) on the water, or HCl solutions of these salts. A deep, blood-red solution is produced, which is decolored by $HgCl_2$.

Silicic Acid. — Salts of this acid constitute a large part of the rock masses of the earth's crust. These salts are all insoluble in water, except those of potassium and sodium. The insoluble salts of this acid are referred to under the insoluble substances (see page 331). The soluble silicates are decomposed by HCl, and when such a solution is treated with HCl, and the solution is evaporated, the silica (SiO_2) is deposited. When the evaporation is completed, this residue of SiO_2 is not again dissolved.

The insoluble silicates are converted into the alkali salts by fusing them with Na_2CO_3. The fused mass then has its alkali

silicate dissolved out and examined by the preceding directions.

A test that may be used as confirmatory of the preceding consists in making a bead of $NaNH_4HPO_4$, and fusing with it the supposed silicate. The fusion should be kept up for some time. If the silicate was present, the metal combined with it unites with the phosphoric acid (a metaphosphate), and the silica, which is set free, remains undissolved in the bead. This may be seen as somewhat irregularly distributed masses in the fused bead.

Tartaric Acid. — Both the tartrates and the solid tartaric acid are decomposed by heat, and become blackened from the free carbon. Carbonates are left if the decomposition is completed. (See under POTASSIUM.) Other organic salts, and organic matter generally, blacken when heated, but in their absence, the presence of tartaric or acetic acids or their salts may be inferred, under these conditions.

When the solid tartrates are heated with H_2SO_4, they are decomposed and blacken, and give off the odor of burning sugar.

Solutions (concentrated) containing tartrates form crystalline precipitates with potassium acetate in the presence of acetic acid. The presence of tartrates prevents the precipitation of group IV. bases, because of the formation of double tartrates of ammonium and the metals of this group. The tartrates are removed by ignition.

Thiosulfuric Acid. — Thiosulfates are all soluble in water, but those of lead, silver, and barium are only sparingly soluble. The double salts of these bases are soluble; *e.g.* $Ag_2S_2O_3$ is quite insoluble, but $AgNaS_2O_3$ is soluble.

The salts of this acid are readily decomposed by acids, the products being a salt of the acid used, SO_2, and sulfur. Consequently, bases do not interfere with the usual test (*i.e.* the decomposition of the salts with H_2SO_4), with the characteristic

products just mentioned. From the acid side comes the interference of the salts of gaseous acids, and especially from the sulfites. The same methods for distinguishing SO_2 may be applied here, as they are under sulfites. The proof of the presence of SO_2, coming from the decomposition of a salt, and accompanied by free sulfur, may be taken as the evidence of the presence of thiosulfates. Whether sulfites accompany or not, the thiosulfates may be determined by the action of lead acetate $(PbC_2H_3O_2)_2$ or silver nitrate $(AgNO_3)$ on the water solution. The solution, after the addition of the reagent, is boiled. The white lead (or silver) thiosulfate is decomposed by water, and PbS(or Ag_2S) and H_2SO_4 are formed. Soluble sulfids will interfere with the result, of course, and must be removed by $ZnSO_4$ before adding these reagents.

The methods that have been given for the recognition of acids do not, of course, cover every possible combination, but if these methods are thoroughly comprehended, the student can, by their combination and use, successfully analyze the mixtures that may be prepared for him.

The method of suggestion and question has not been used in this study of the acids, but the learner should not fail to master thoroughly the chemical changes in these tests, and to write all the reactions indicated. The rule should be, at this stage of the work, never to make a test for its own sake, but for the insight it may give into the character of chemical action.

It may be noted finally that the knowledge of what acids are present in a given mixture is helpful in deciding about the bases that may be combined with these acids. For example, the knowledge that phosphates are present in the water solution of a substance would enable the analyst to decide that no group III. or IV. base can be present, provided tartrates are absent.

For confirmation of the results obtained by the methods given, see study of each acid, Part I.

APPENDIX.

THE following table of atomic masses was prepared by F. W. Clark, and is made on the basis of Oxygen = 16. The table includes the latest corrections. In the atomic masses used in the text of this work hydrogen is unity.

NAME.	ATOMIC MASS.	NAME.	ATOMIC MASS.
Aluminium	27.	Neodymium	140.5
Antimony	120.	Nickel	58.7
Arsenic	75.	Nitrogen	14.03
Barium	137.43	Osmium	190.8
Bismuth	208.9	Oxygen	16.
Boron	11.	Palladium	106.6
Bromin	79.95	Phosphorus	31.
Cadmium	112.	Platinum	195.
Cæsium	132.9	Potassium	39.11
Calcium	40.	Praseodymium	143.5
Carbon	12.	Rhodium	103.
Cerium	140.2	Rubidium	85.5
Chlorin	35.45	Ruthenium	101.6
Chromium	52.1	Samarium	150.
Cobalt	59.	Scandium	44.
Columbium	94.	Selenium	79.
Copper	63.6	Silicon	28.4
Erbium	166.3	Silver	107.92
Fluorin	19.	Sodium	23.05
Gadolinium	156.1	Strontium	87.6
Gallium	69.	Sulfur	32.06
Germanium	72.3	Tantalum	182.6
Glucinum	9.	Tellurium	125.
Gold	197.3	Terbium	160.
Hydrogen	1.008	Thallium	204.18
Indium	113.7	Thorium	232.6
Iodin	126.85	Thulium	170.7
Iridium	193.1	Tin	119.
Iron	56.	Titanium	48.
Lanthanum	138.2	Tungsten	184.
Lead	206.95	Uranium	239.6
Lithium	7.02	Vanadium	51.4
Magnesium	24.3	Ytterbium	173.
Manganese	55.	Yttrium	89.1
Mercury	200.	Zinc	65.3
Molybdenum	96.	Zirconium	90.6

The student should fill the spaces as he determines the solubilities in course of hi
For completeness of the table the spaces may be filled by consulting the proper auth
name of the acid that is best used for this purpose. It is well to restrict the acid
method. The solubilities in water may be denoted as follows: I. = insoluble; S. =

	Silver	Mercury(-ous)	Mercury(-ic)	Lead	Bismuth	Copper	Cadmium	Tin(-ous)	Tin(-ic)	Antimony	Iron(-ous)	Iron(-ic)	Aluminium
Acetate	S	S	PS	S	S	S	S	S	S	S	S	S	S
Arsenate	HNO_3												
Arsenite	HNO_3												
Borate													
Bromid													
Carbonate													
Chlorate													
Chlorid													
Chromate													
Cyanid													
Ferricyanid													
Ferrocyanid													
Fluorid													
Fluosilicate													
Hydroxid													
Hypochlorite													
Iodate													
Iodid													
Nitrate													
Nitrite													
Oxalate													
Oxid													
Permanganate													
Phosphate													
Silicate													
Sulfate													
Sulfid													
Sulfite													
Sulfocyanate													
Tartrate													
Thiosulphate													

study of salts. Spaces are left for a few salts that he will not usually prepare. rity. In case the salt is not soluble in water, the space may be filled with the ısed to nitric and hydrochloric acids. A few spaces are filled to illustrate the luble; P.S. = partially soluble.

Chromium . . .	Cobalt	Nickel	Manganese . .	Zinc	Barium	Strontium . . .	Calcium	Magnesium . .	Potassium . . .	Sodium	Ammonium . .	
S	S	S	S	S	S	S	S	S	S	S	S	Acetate.
												Arsenate.
												Arsenite.
												Borate.
												Bromid.
												Carbonate.
												Chlorate.
												Chlorid.
												Chromate.
												Cyanid.
												Ferricyanid.
												Ferrocyanid.
												Fluorid.
												Fluosilicate.
												Hydroxid.
												Hypochlorite.
												Iodate.
												Iodid.
												Nitrate.
												Nitrite.
												Oxalate.
												Oxid.
												Permanganate.
												Phosphate.
												Silicate.
												Sulfate.
												Sulfid.
												Sulfite.
												Sulfocyanate.
												Tartrate.
												Thiosulphate.

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